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CONTENTS

PROCEEDINGS OF THE SOCIETY—

THE EFFECT OF DISPERSOL VL ON THE DYEING PROPERTIES OF VAT DYES ON VISCOSE RAYON (*R. W. Speke*) 569

SOME RELATIONS, ECONOMICAL AND TECHNICAL, BETWEEN THE PULP AND PAPER TRADE AND THE TEXTILE TRADE (*G. Ullmann*) 576

COMMUNICATIONS—

THE APPLICATION OF 5-BISALKOXYMETHYLUREAS (DIALKYL ETHERS OF DIMETHYLOLUREA) TO WOOL (*P. Alexander, D. Carter, and C. Earland*) 579

THE ACTION OF CHLORINE DIOXIDE ON WOOL (*D. B. Das and J. B. Speakman*) 583

CORRESPONDENCE 588

NOTES 588

OBITUARY NOTICE 589

NEW BOOKS AND PUBLICATIONS 589

REPORTS ON GERMAN INDUSTRY 592

ABSTRACTS 593

THE SOCIETY OF DYERS AND COLOURISTS 32-34 PICCADILLY BRADFORD YORKS

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MANCHESTER SECTION

Meeting held in the Gas Showrooms, Town Hall Extension, Manchester, on 21st April 1950, Mr. R. J. HANNAY in the chair

The Effect of Dispersol VL on the Dyeing Properties of Vat Dyes on Viscose Rayon

R. W. SPEKE

It has been shown that the restraining effect of Dispersol VL upon leuco vat dyes is a function of the *amount* present in the system and not of its concentration in the aqueous solution. A method of assessment of the relative sensitivities of individual leuco vat dyes has been evolved. By this method the relationship between the dyebath exhaustion and the amount of Dispersol VL in the dyebath, obtaining under given dyeing conditions, is experimentally determined. A sensitivity factor is then calculated from the slope of the initially linear graphical relation between these two variables. An anomalous behaviour has, however, been encountered with certain indanthrone derivatives. Evidence is presented to show the influence, on restraining effect, of varying the depth of shade, the temperature of dyeing, and the salt concentration of the dyebath.

Investigations into the retarding and levelling effects of this non-ionic body, as herein reported, indicate that these two properties are related to the restraining effect of Dispersol VL upon the leuco vat dye under consideration.

The high affinity of leuco vat dyes for cellulosic fibres has promoted a considerable amount of research into modifications of, or alternatives to, the traditional dyeing processes, with a view to obtaining results of greater uniformity. Among the many possibilities is the use of dyebath assistants, ambiguously described as levelling, retarding, or restraining agents. One of these products is Dispersol VL, an aqueous solution of a fatty alcohol–ethylene oxide condensate, the value of which, as an aid to the production of level and well penetrated dyeings on an industrial scale, has been well proven. In order to facilitate the efficient use of Dispersol VL in practical vat dyeing a detailed study has been made of its effect on the dyeing properties of leuco vat dyes on viscose rayon. This has involved a separate investigation into the three possible functions of the non-ionic body as a vat-dyebath adjuvant, viz.—

(1) Restraining effect, i.e. the retention of a certain amount of dye permanently in solution

(2) Retarding effect, i.e. a reduction in the rate of transfer of dye from solution to fibre

(3) Levelling effect, i.e. a promotion of the rate of migration of absorbed leuco dye from fibre to fibre.

It is convenient to consider the restraining, retarding, and levelling effects separately.

I—Restraining Effect

EFFECT OF CONCENTRATION OF DISPERSOL VL

Two methods are normally employed for defining the quantity of Dispersol VL present in a leuco vat dyebath, viz.—

(*a*) As a concentration, based on the volume of the dyebath

(*b*) As an amount, expressed most conveniently as a percentage on the weight of the fibre being dyed.

In order to assess which of these methods was preferable, dyeings of Caledon Gold Orange G and Caledon Jade Green XN were prepared in liquor : goods ratios of 10–200 : 1 under three different series of conditions—

(1) No Dispersol VL

(2) Constant concentration of Dispersol VL based on dyebath volume

(3) Constant amount of Dispersol VL, i.e. a constant percentage based on the weight of viscose rayon.

The dyebath exhaustions, both here and subsequently, were measured on the Hilger Spekker absorptiometer, using an unpublished method developed by Fowler and Michie. This is based upon comparative measurements of the leuco

solutions suitably diluted with a "medium" containing per litre—

7·5 c.c. Dispersol VL
30 c.c. Caustic soda 68°Tw.
12 g. Sodium hydrosulphite

The results of this experiment are shown in Fig. 1 and 2. From these curves it will be apparent

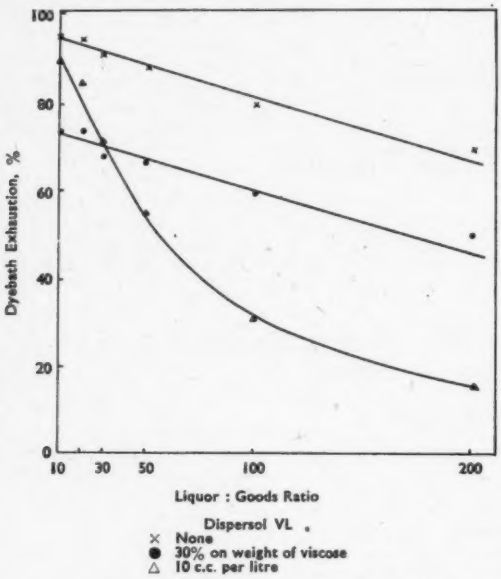

FIG. 1—Effect of Dispersol VL on Exhaustion of Caledon Gold Orange G

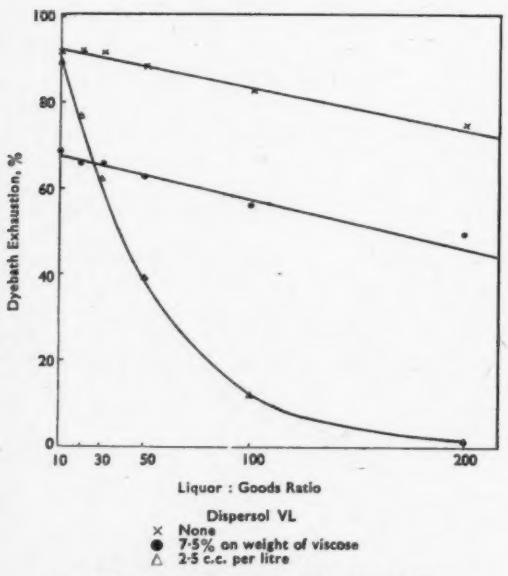

Fig. 2—Effect of Dispersol VL on Exhaustion of Caledon Jade Green XN

that, with a given concentration of Dispersol VL in the dyebath, a greater restraining effect is realised as the liquor ratio is increased. On the other hand, if a constant amount of Dispersol VL is present, the lowering of exhaustion occasioned by its introduction is not materially affected by very wide differences in liquor ratios. For this reason the latter method of definition has been used throughout this work.

SENSITIVITY OF INDIVIDUAL DYES

The sensitivity of individual leuco vat dyes to the restraining effect of Dispersol VL was then compared on commercial 150-denier 27-filament viscose rayon yarn by measuring the percentage dyebath exhaustion obtained with various quantities of Dispersol VL in the dyebath. A standard series of conditions was employed throughout, comprising—

Dye	10% Single strength (on weight o viscose rayon)
Liquor ratio	30 : 1
Time of dyeing	1 hr.
Temperature of dyeing ...	60°c. throughout
Dispersol VL	0–30% on the weight of viscose rayon

Two distinct types of behaviour were encountered throughout the range of homogeneous vat dyes. These can be described as—(*a*) *normal behaviour*, where the addition of increased amounts of Dispersol VL to the dyebath brought about a progressive reduction in the exhaustion of the dyebath; and (*b*) *anomalous behaviour*, where the addition of small amounts of Dispersol VL gave a minimal exhaustion, but on further increasing the initial addition of Dispersol VL a higher degree of exhaustion was realised. The two distinct types of behaviour are most conveniently considered separately.

(A) NORMAL BEHAVIOUR

The results of this examination are shown in Table I. The significance of the column headed *s* will be discussed later.

When these results were expressed graphically it was apparent that, with the exception of Caledon Khaki R, a straight-line relationship existed between percentage dyebath exhaustion and the percentage of Dispersol VL (calculated on the weight of viscose rayon) in the bath. Typical results are shown in Fig. 3 and 4. With very sensitive dyes, however, the linear relation reaches a limit, beyond which a higher degree of exhaustion is realised than if the initial slope of the line were maintained, as shown in Fig. 5.

The straight line passing through the maximum number of experimental points having been constructed, a measure of the slope of the linear portion of the curve (and hence of the sensitivity of individual dyes) was obtained by substitution in the formula—

$$E_0 - E_D = sD$$

where E_0 = Dyebath exhaustion (%) with no Dispersol VL in the bath

E_D = Dyebath exhaustion (%) with D% Dispersol VL (on the weight of viscose rayon) in the bath

s = Sensitivity factor, a constant for each individual dye.

The constant s, which can be calculated from this equation, represents the lowering of exhaustion occasioned by the introduction of 1% Dispersol

TABLE I

Dispersol VL (% on wt. of viscose) ...			0	1·0	2·5	5·0	10	20	30
Caledon Dye		*s*	Dyebath Exhaustion (%)						
Yellow 5GK ...	...	0·23	68·0	68·6	68·7	69·8	66·4	64·0	62·6
Yellow 5G ...	...	0·35	91·2	92·7	91·5	89·0	87·5	86·8	80·5
Yellow GN ...	...	0·50	95·0	95·2	94·8	93·7	91·7	87·3	79·8
Yellow 4G ...	...	0·14	81·9	—	84·0	82·0	82·0	80·8	76·2
Yellow 2R ...	...	0·37	77·6	78·6	77·2	76·8	75·2	71·2	67·5
Gold Orange G ...		0·85	94·2	94·2	92·8	91·6	84·3	77·6	67·5
Gold Orange 3G ...		0·67	89·3	88·8	88·2	87·6	83·8	77·4	68·8
Orange 2RT		2·1	93·1	91·3	88·6	82·8	72·6	59·7	51·0
Brilliant Orange 4RN...		3·0	89·0	81·8	82·6	76·0	58·5	42·0	29·0
Brilliant Orange 6R ...		0·55	74·4	73·6	75·0	73·0	71·2	62·6	58·5
Red 2G		0·23	79·6	78·4	77·6	77·0	75·8	74·2	72·2
Red 5G		0	62·9	63·6	65·8	65·2	63·8	62·0	62·0
Pink RL		0	72·7	74·3	72·1	74·6	73·1	72·8	70·8
Red BN		0·67	88·4	—	—	85·2	82·4	75·8	67·4
Brilliant Red 3B ...		0·12	95·8	95·8	95·8	95·0	93·9	93·7	92·2
Red X5B		2·3	68·1	69·4	65·5	56·4	47·0	36·5	24·5
Red Violet 2RN ...		1·2	74·8	73·5	70·6	65·8	59·0	50·0	37·0
Brilliant Purple 4RP...		2·7	95·9	95·2	90·3	81·2	68·6	54·2	43·0
Brilliant Violet 3R ...		1·7	64·0	66·4	61·2	60·0	53·5	33·5	27·5
Brilliant Violet R ...		1·2	76·5	76·4	76·5	73·2	63·6	52·4	41·2
Dark Blue 2R ...		2·9	93·2	90·0	86·6	80·2	62·8	45·3	30·0
Violet XBN ...		0	88·3	88·6	85·5	83·6	85·5	86·8	86·7
Navy Blue 2R ...		7·0	96·3	83·5	68·2	47·5	24·0	14·5	4·0
Dark Blue G		2·3	87·7	86·7	82·5	75·6	65·4	52·5	34·5
Brilliant Blue RN ...		0·28	92·0	92·7	92·2	94·5	90·1	87·5	85·2
Blue GCP		0·43	89·5	89·1	85·7	84·4	83·5	82·4	76·0
Brilliant Blue 3G ...		0·30	92·3	90·5	92·0	89·8	90·3	87·0	83·0
Green 2B		0·63	91·5	85·6	86·8	85·5	85·8	80·2	70·6
Green BN		1·2	95·2	92·3	90·9	87·8	80·7	70·8	60·4
Green RC		15	87·2	69·4	51·5	37·2	27·2	22·0	10·0
Olive Green B ...		1·0	95·8	95·8	93·9	89·3	85·0	75·6	67·0
Green 7G		0·47	91·2	88·9	88·0	87·7	83·0	80·8	76·9
Jade Green 2G ...		5·5	92·4	88·2	78·2	62·3	38·0	20·8	17·5
Jade Green XN ...		3·4	96·5	94·2	91·6	82·7	62·7	48·8	41·0
Jade Green 3B ...		8·8	95·0	85·7	71·5	51·5	28·5	16·5	12·5
Orange Brown 2G ...		1·0	90·8	91·1	89·3	88·8	80·4	70·3	62·3
Dark Brown 6R ...		1·3	79·9	75·9	75·2	70·0	64·2	54·0	38·5
Brown 3G		1·5	78·2	79·4	77·0	74·4	60·2	49·5	37·0
Dark Brown 2G ...		1·7	75·5	70·3	70·0	66·0	55·5	39·5	30·0
Brown R		0·33	78·0	79·2	79·0	78·5	77·0	73·0	67·4
Dark Brown 3R ...		0·3	91·8	91·0	90·4	90·0	88·3	86·2	81·8
Olive D		1·4	87·6	89·0	86·7	82·2	69·6	61·8	49·5
Khaki R		—	45·3	42·5	38·4	35·5	30·0	29·5	25·5
Khaki 2G		0·1	63·0	59·5	61·2	61·2	60·4	60·5	59·0
Olive R		0·63	85·0	81·8	81·8	80·0	76·8	73·0	64·6

VL (calculated on the weight of viscose rayon) into the dyebath, and provides a numerical comparison of the sensitivities of the individual dyes to the restraining effect of Dispersol VL. The values of *s* for the various dyes are shown in Table I.

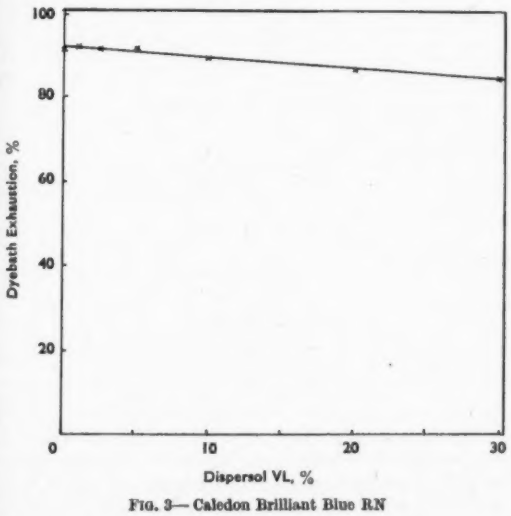

FIG. 3—Caledon Brilliant Blue RN

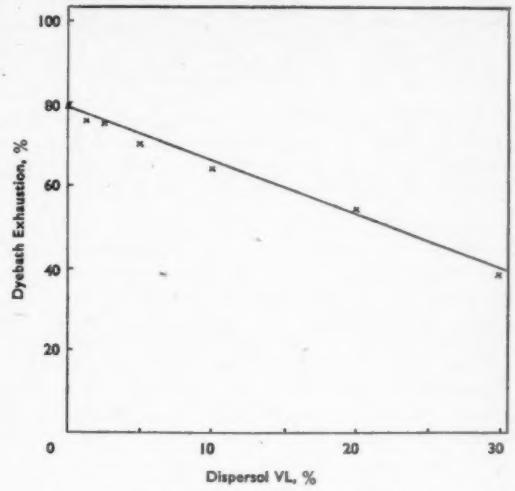

FIG. 4—Caledon Dark Brown 6R

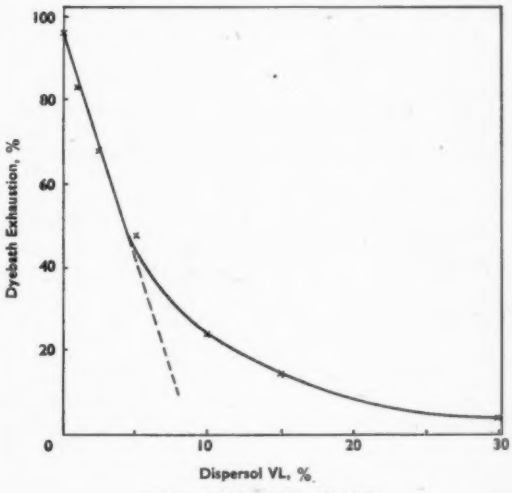

FIG. 5—Caledon Navy Blue 2R

CORRELATION BETWEEN VAT DYE CONSTITUTION AND SENSITIVITY TO DISPERSOL VL

No sweeping generalisations can be made upon the correlation between chemical constitution and sensitivity to Dispersol VL. Certain tendencies are, however, clearly defined. The introduction of halogen atoms into any given nucleus produces a dye of increased sensitivity to Dispersol VL, as indicated by the data in Table II.

TABLE II

Caledon Dye	Constitution	Sensitivity *s*
Gold Orange G ...	Pyranthrone	0·85
Orange 2RT ...	Dibromopyranthrone	2·1
Brilliant Orange 4RN	Tribromopyranthrone... ...	3·0
Jade Green XN ...	Dimethoxydibenzanthrone ...	3·4
Jade Green 2G ...	Brominated dimethoxydibenzanthrone	5·5

It does not follow, however, that a dye containing halogen atoms will be very sensitive to Dispersol VL, as is shown in Table III.

TABLE III

Caledon Dye	Constitution	Sensitivity s
Brilliant Orange 6R	Dibromoanthanthrone ...	0·55
Blue GCP	Chlorinated indanthrone ...	0·43
Green 2B	Dichlorodiaminoindanthrone...	0·63

There is, unfortunately, insufficient evidence to indicate what effect other substituents in the dye molecule, such as amino, nitro, or hydroxy groupings, exert upon sensitivity to Dispersol VL.

Of the main constitutional groups of dyes, it is possible to generalise upon the behaviour of only one such group, viz. dibenzanthrone and its derivatives. Of nine dyes of this class examined, eight are classified as "extremely sensitive" to Dispersol VL. The anthraquinone–carbazole derivatives vary widely in their sensitivities. However, the magnitude of the s factor for certain analogous members of this series shows that similar chemical structures have similar sensitivities.

TABLE IV

Dibenzoylaminodianthraquinone–carbazoles

Caledon Dye	Sensitivity s
Gold Orange 3G ...	0·67
Olive B	0·63
Brown R	0·33

Anomalous results, which are not easy to explain, are found in comparing the s factor for a number of very similar chemical entities (Table V).

TABLE V

Caledon Dye	Constitution	Sensitivity s
Red 5G	1:4-Dibenzoylamino-anthraquinone ...	0
Red X5B	1:4:5-Tribenzoylamino-anthraquinone ...	2·3
Jade Green XN ...	Dimethoxydibenzanthrone	3·4
Jade Green 3B... ...	Diethoxydibenzanthrone ...	8·8

MECHANISM OF RESTRAINING EFFECT

Finally, it is necessary to consider the mechanism of the restraining action of Dispersol VL upon the leuco vat dyes. A limited number of experiments indicate that Dispersol VL has no affinity for viscose rayon from neutral solutions even under a variety of conditions of temperature and electrolyte concentration. Any interaction between the non-ionic body and the leuco vat dye must therefore take place in the aqueous phase. The classical assumption supposes that hydrogen bond formation is the cause of the mutual affinity of the leuco vat dye and the non-ionic body. Thus Chwala in his book *Textilhilfsmittel*[1] states that—

> Peregal O [which is chemically very similar to Dispersol VL] and Peregal OK form insoluble addition compounds with phenols and compounds containing phenolic hydroxyl groups, e.g. tanning agents. It can be assumed, therefore, that with vat dyes similar compounds are formed by hydrogen bonding. Valko [2] has measured the degree of increased aggregation of the leuco salt obtained with Indanthren Brilliant Green FBB [Caledon Jade Green XN]—see the following Table.

[TABLE VI]

No. of Experiment	Constitution of the Dyebath	Mol. Wt. of Particles	Degree of Aggregation
1	0·01% Indanthren Brilliant Green FBB, 0·2 N-NaOH + 0·5% $Na_2S_2O_4$	1700	3
2	As (1) + 0·3% Peregal O ...	220,000	420

> Peregal O and Peregal OK act as levelling agents because they have an affinity for the dyes. They serve as nuclei for the formation of larger aggregates of leuco salts, which lower the initial rate of absorption of certain vat dyes by fibres.

The linear relation between the amount of Dispersol VL in the dyebath and the percentage dyebath exhaustion tends to confirm the view that there is a definite addition compound formed between the non-ionic body and the leuco vat dye. However, it must be emphasised that the conditions of measurement do not represent the establishment of *true* equilibrium, although being sufficiently final for all practical purposes. The extreme individuality of each leuco vat dye to the restraining effect of Dispersol VL can only be attributed to the inability of certain diketone structures to bond with the ethylene oxide chain. However, before any definite conclusion as to the exact nature of the dye–Dispersol VL complexes could be arrived at, a study of a wider series of simple analogous vat dyes would have to be undertaken.

EFFECT OF DYEBATH CONDITIONS ON RESTRAINING EFFECT

The next step in this investigation was to determine the effect of varying dyebath conditions upon the restraining effect of Dispersol VL with those dyes showing a "normal" type of behaviour. The variables examined were depth of dyeing, temperature, and electrolyte concentration.

DEPTH OF DYEING—As the quantity of dye present in the dyebath decreases, a proportionately greater restraining effect is realised by the introduction of a given quantity of Dispersol VL. This effect is very much accentuated with extremely sensitive dyes, as shown in Fig. 6.

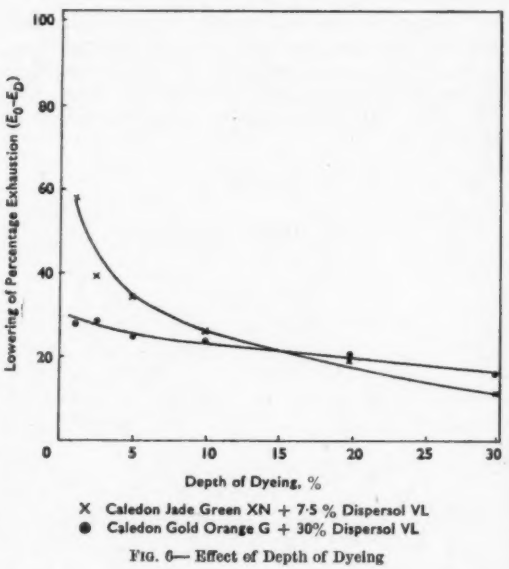

FIG. 6—Effect of Depth of Dyeing

TEMPERATURE—The effect of temperature on the exhaustion of selected vat dyes was measured, with and without addition of Dispersol VL to the dyebath, over the range 20–80°C. The results

showed that there is no general relation between temperature and restraining effect; e.g. Caledon Green RC is much more markedly restrained at low temperatures than at high temperatures, but with Caledon Red Violet 2RN little variation with temperature is apparent.

ELECTROLYTE CONCENTRATION— The s factors for various Method 2 and 3 dyes were determined as previously described, but with an addition of 10 g. of sodium chloride per litre of dyebath. The results so obtained showed that an almost parallel displacement of the curve resulted from the addition of salt.

Qualitative tests with extremely sensitive dyes showed that in presence of excessive quantities of Dispersol VL the addition of large quantities of sodium chloride did not materially improve the degree of dyebath exhaustion realised. Electrolyte addition, therefore, cannot be used to neutralise an excessive restraining effect.

(B) ANOMALOUS BEHAVIOUR

Three of the dyes examined, viz. Alizanthrene Blue RC, Caledon Blue RC, and to a less extent Caledon Brilliant Violet 3B, showed a completely anomalous dyeing behaviour in presence of Dispersol VL. For example, under the conditions used for the determination of the s factor as previously described, the results shown in Table VII were obtained.

TABLE VII

Dispersol VL (% on wt. of viscose)	0	1·0	2·5	5·0	10	20	'30
Dye	Dyebath Exhaustion (%)						
Alizanthrene Blue RS (one experiment) ...	83·0	19·5	16·0	22·2	27·7	36·0	43·4
Caledon Blue RC (mean of two experiments)	91·2	14·7	12·1	13·0	13·5	21·7	30·0
Caledon Brilliant Violet 3B (mean of two experiments)	94·6	64·8	49·3	59·8	59·0	49·5	42·2

Thus an initial marked lowering of exhaustion was obtained, on the introduction of a very small amount of Dispersol VL, followed by a subsequent increase in exhaustion with higher amounts of the non-ionic body. Furthermore, with additions of Dispersol VL of the order of 1–2% (based on the weight of viscose rayon) a finely divided precipitate was apparent in the dyebath, whereas when the amount of Dispersol VL added initially was greater than 10% (on the weight of viscose rayon) this precipitate was not produced.

A closer study of this phenomenon was therefore undertaken with Caledon Blue RC. It must be stated, however, that it was generally found to be very difficult to obtain reproducible quantitative results with this dye. Nevertheless, it was clearly shown that the restraining effect produced was not only a function of the quantity of Dispersol VL present but also of the caustic soda and dye concentrations in the dyebath.

The relation between dyebath exhaustion and the amount of Dispersol VL present in the dyebath was measured, under the conditions previously used for the determination of the s factor, but with an increase in the initial caustic soda content of the dyebath. The results obtained with Caledon Blue RC are shown in Fig. 7.

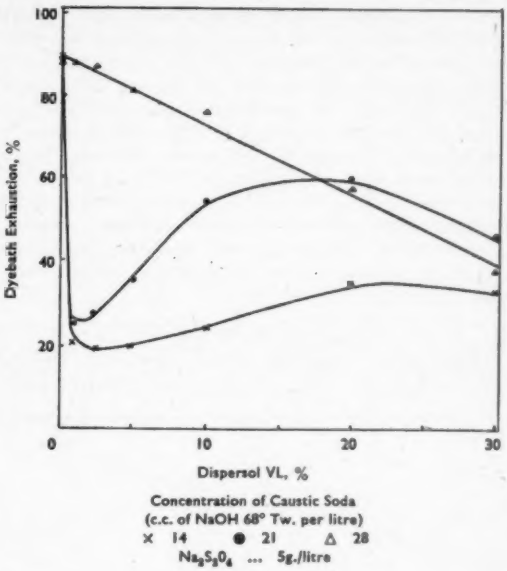

FIG. 7— Caledon Blue RC

By using twice the normal quantity of caustic soda in the preparation of the leuco solution, therefore, a normal type of restraining effect is obtained with Caledon Blue RC, the s factor being 1·6. A similar result was obtained with Alizanthrene Blue RC ($s = 1·3$). With Caledon Brilliant Violet 3B, however, no significant change in the shape of the exhaustion–Dispersol VL graph occurred on increasing the initial caustic soda concentration of the dyebath. It must be emphasised that the increased exhaustion resulting from the use of excess caustic soda in dyebaths containing leuco Caledon Blue RC and Dispersol VL can be obtained only if the extra caustic soda is added to the dyebath before the Dispersol VL. If dyeing is commenced with a low caustic soda concentration, and then excess alkali added to the dyebath during the dyeing process, very little increase in exhaustion is obtained.

With Caledon Blue RC it was found that, as the concentration of dye in the dyebath was increased, i.e. with an increase in the depth of dyeing or a decrease in the liquor ratio, the tendency for precipitation of the leuco dye to take place in presence of Dispersol VL increased. For example, in dyebaths containing 5% Dispersol VL (based on fibre weight) in a 30 : 1 liquor ratio, increased concentrations of caustic soda were required to prevent leuco dye precipitation as the depth of dyeing was increased, as indicated in Table VIII.

TABLE VIII

Standard Dye (% on fibre weight)	Minimum NaOH Concentration (c.c. NaOH 68°Tw. per litre)
2·5	15
10	25
25	30

Although the so-called anomalous type of behaviour is of considerable theoretical interest, it is possible from this work to advance only the most

tentative explanation of these phenomena. However, it seems possible that, if the affinity between Dispersol VL and the leuco vat dye were extremely high, when a small amount of the non-ionic body is added to the leuco solution, aggregates of low solubility would be formed. Where the number of molecules of Dispersol VL per molecule of the leuco compound in the complex is high, it might be expected that a product of greater solubility and hence greater dyeability would be formed. Insoluble complex formation can, however, offer no explanation of the effect of increased caustic soda concentration.

II—Retarding Effect

The ideal retarding effect, whereby dye is absorbed by the fibre more slowly but to the same ultimate degree of exhaustion from dyebaths containing Dispersol VL, can never be completely realised. However, with certain dyes a close approximation to this ideal can be attained by combining temperature control with the use of the non-ionic body. The enhanced retarding effect of Dispersol VL at low temperatures is shown quite clearly in Fig. 8 and 9.

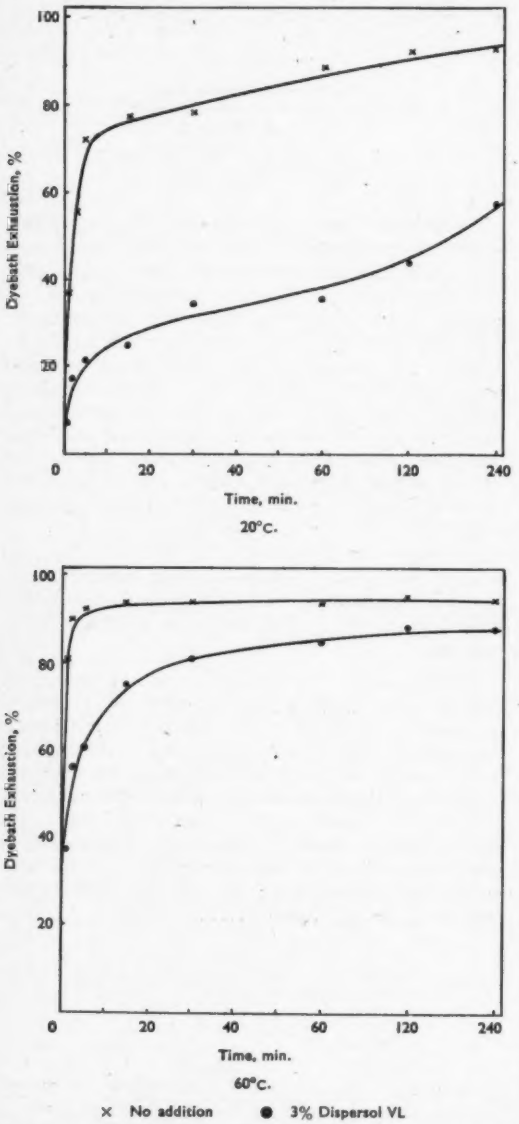

FIG. 8 and 9—Caledon Jade Green XN at 20° and 60°C. respectively

It will be recalled, however, that the variation in restraining effect with temperature is diverse, and it is therefore to be anticipated that an analogous diversity will be encountered with retarding effect at different temperatures. This was confirmed in that with Caledon Red Violet 2RN the lowering in the rate of dye uptake occasioned by the introduction of Dispersol VL is no greater at 20° than at 60°C. An analysis of this problem shows that, when Dispersol VL functions efficiently as a vat retarding agent at low temperatures with any particular dye, that dye must—

(*a*) Be capable of interacting with Dispersol VL, i.e. have a high *s* factor; and

(*b*) Retain its affinity for viscose rayon even at high temperatures.

III—Levelling Effect

On a basis of white skein levelling tests it can be demonstrated that Dispersol VL definitely improves the levelling properties of leuco vat dyes.

Selected vat dyes applied to 150/27 viscose rayon yarn were treated in blank dyebaths for 1 hr. at 60° and 80°C. respectively. In one case an addition of 5% Dispersol VL (on the total weight of viscose rayon) was made to the levelling bath. A comparison of the enhanced migration occasioned by the introduction of Dispersol VL showed that—

(i) A greater improvement was realised at 60° than at 80°C.

(ii) In general the higher the *s* factor the greater was the magnitude of the dye migration.

This would indicate that there is a distinct, if not exact, correlation between restraining effect and levelling effect. Dispersol VL would therefore appear to function as a levelling agent by increasing the amount of dye removed from the originally dyed fibre by the reducing solution, and this dye then becomes available to the white material.

Conclusions

(i) The restraining effect of Dispersol VL in a leuco vat dyebath is a function of the amount present in the system and not of its concentration.

(ii) The sensitivity of leuco vat dyes to the restraining effect of Dispersol VL varies greatly, being most effectively compared by constructing the exhaustion–Dispersol VL curve under any given conditions of time, temperature, and electrolyte concentration. The linearity of this relationship affords a reasonably accurate quantitative measurement of relative sensitivities.

(iii) Alizanthrene Blue RC, Caledon Blue RC, and to a less extent Caledon Brilliant Violet 3B show an entirely anomalous type of relationship. A maximum restraining effect is obtained with these dyes with small amounts of Dispersol VL.

(iv) The restraining influence of any given quantity of Dispersol VL is proportionately higher in pale shades than in heavy shades.

(v) The addition of small amounts of sodium chloride to leuco vat dyebaths does not materially alter the sensitivity to Dispersol VL.

(vi) The effect of temperature upon the exhaustion of dyebaths in presence of Dispersol VL varies according to the nature of the individual dye. There is, however, a general tendency for the maximum effect to be exerted at low temperatures.

(vii) Dispersol VL improves the migration of leuco vat dyes. There is a distinct correlation between improvement in levelling and restraining effect.

The author would like to thank those of his colleagues who have participated in this investigation, in particular Mr. L. Robishaw, who has undertaken all the experimental work herein recorded.

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[2] Valko, *Trans. Faraday Soc.*, **31**, 230 (1935).

Discussion

Mr. J. Holt: Do the same principles hold good on types of cellulose— cotton, linen, cuprammonium, etc.— other than viscose rayon?

Mr. Speke: The *s* factor has also been determined with five dyes on bleached cotton and cuprammonium rayon under identical conditions to those employed with viscose rayon. The magnitude of *s* for each dye is by no means identical on all three fibres, probably because the conditions used in the assessment do not permit the establishment of true equilibrium. Qualitatively, however, the results of this limited evaluation show that there is a close similarity between the restraining effect obtained on the three fibres; e.g. a dye which was "virtually insensitive" on viscose rayon is not markedly restrained on either cotton or cuprammonium rayon.

Mr. Holt: In using products of the Dispersol VL type and those retarding the rate of dyeing, the criticism is frequently heard that a large proportion of the dye remains in the dyebath and that yields are, therefore, low. Is it possible to obtain this retarding–levelling effect, and then at a given stage in the dyeing gradually release this influence and allow exhaustion to take place? If so, what products would the lecturer recommend for this purpose?

Mr. Speke: It is, of course, possible to neutralise the restraining effect of Dispersol VL by the addition of e.g. sulphonated auxiliary products such as Turkey Red Oil and Calsolene Oil HS. It has generally been found, however, that there is very little advantage to be gained— from the level dyeing point of view— from this approach, possibly because it is impossible to achieve a *gradual* neutralisation of the restraining effect.

Dr. C. M. Whittaker: How soon is the dyeing commenced after the addition of Dispersol VL to the prepared vat? It has been my experience in using sulphite cellulose waste liquor as a retardant that it makes a very big difference in the depth of shade obtained if one does not enter the material almost immediately after the retardant has been added.

Mr. Speke: In all experiments the dye had been vatted and diluted to dyebath concentration, and the solution allowed to stand for 15 min. at the ultimate dyeing temperature. The Dispersol VL, suitably diluted with water, was then added to the dyebath, followed as quickly as possible by the yarn. No experiments have been undertaken, in this investigation, to show whether the time lag between adding the non-ionic body and entering the yarn is of importance with Dispersol VL, although it is a general recommendation that this time interval should be reduced to a minimum.

Dr. P. W. Cunliffe: The precipitation of dyes such as Caledon Blue RC by the ethylene oxide long-chain compounds appears to be general. With regard to the use of Dispersol VL as recommended by the lecturer one would have thought it would be much better to enter it into the bath before adding the dye rather than *vice versa*.

Mr. Speke: This is quite feasible, always providing that the vatted dye, as added to the dyebath, is in true solution. With dyes such as Caledon Blue RC, where intrinsically the solubility of the leuco dye is low, the stock vat is frequently not a true solution. A process of solubilisation must then take place on dilution to dyebath volume. It is to be anticipated in such cases that, if the non-ionic body is added to the dyebath prior to addition of the vatted dye, this process of solubilisation will be retarded or prevented. It is interesting to note in this connection that, in these laboratory experiments the best degree of reproducibility is obtained with the anomalous-type dyes when they are vatted *in full volume* in presence of Dispersol VL.

MANCHESTER SECTION

Meeting held at the Gas Department Showrooms, Manchester, on 21st October 1949, Mr. R. J. HANNAY in the chair

Some Relations, Economical and Technical, between the Pulp and Paper Trade and the Textile Trade

G. ULLMANN

(Read by P. BEAN)

Paper and textiles are both commodities of the first importance and face a great development in the future. Thus the total world production in 1948 of cotton, wool, silk, and rayon amounted to 17·8 thousand million pounds, of which cotton accounted for 73%, wool 13%, rayon 14% and silk was negligible[1], whereas in 1922–1928 rayon was only 1% of the total fibre consumption. The total fibre consumption of 1948 was over 14% more than in the previous year, and was the highest since 1940. On an assumed present world population of 2,300 million people, this would mean that the average consumption of these four textile fibres was about 7½ lb. per head per year. But this is less interesting than the fact that each of the 145 million inhabitants of the U.S.A. consumed about 32 lb. per year. If this is compared with the 2–3 lb. per head in some other countries with greater populations, the great increase which should accompany the development of those countries can be visualised.

Taking the production of paper of all kinds in 1948 as about 78 thousand million pounds of pulp, about 32 lb. was used per head of the world population. The U.S.A. has consumed about 350 lb. per head, or practically two-thirds of the world's total production, leaving only about 11 lb. per head for the rest of humanity.

In view of the enormous difference between the consumption of textile fibres and paper in the United States and the rest of the world, an immense growth in the total consumption of both commodities can be expected.

Paper has now started and continues with great speed to invade the province of textiles, and it seems to be a most successful invader, well supported by its cheapness. Thus sacks used to be mainly constructed of jute, but in the United States and elsewhere this has been largely replaced by paper. This was much more effective when it was found how to protect the paper by impregnation against the influence of water, moulds, insects, etc. The effectiveness of the present type of cement bags is one of the best examples. Further, 60% of America's domestic flour is packed in paper; but in the last case the position is being changed by millers packing flour in bags made of printed cotton fabric, which can be used for dresses or domestic purposes.

Sometimes the invader — paper — has first advanced and later been repelled. Thus at the time of World War I twisted paper yarns were made to serve for clothing, cartridge belts, sandbags, camouflage nets, etc. This was a necessary but unsuccessful venture as far as clothing fabrics were concerned. In England and France paper yarns were used as a backing for Wilton-type and other carpets; they are still in use for this purpose, and it is claimed that they are in some ways superior to jute. The doom of paper-thread for clothing was sealed by rayon. It took only a few years for the very great technical developments to use the same basic cellulosic material to produce man-made fibres, and these have steadily improved in quality and have become cheaper than cotton.

Man-made fibre (14% of the world fibre consumption) requires about three times its weight of the raw material, and since fibre consumption will grow enormously, it will be seen that there will be at least some competition for the starting material between paper and these textiles. Point is given to this remark by statements from the recent F.A.O. conference in Montreal that there is not enough wood available to satisfy the paper industry. If the probable enormous need for fibres in the not too distant future is considered, and it is asked from what source they can be supplied for both pulp and textiles, it will appear that the soil will be unable to fill the gap, which increases with time. Man-made fibres will have to do that. The chemical pot is elastic, Nature is not.

Very large quantities of paper towels are used; crêped paper handkerchiefs have an obvious place, and in many circumstances are more desirable than textiles. In the same line are the varieties of toilet tissues. Duster material of special grades of paper is used for cleaning furniture, glass, and metal, and some varieties can be used either wet or dry, having been suitably treated with melamine resins or the like. Pillows made of paper and stuffed with shredded paper are now coming into use on British Railways; this was a French idea, and is now used in many places. The railways have also adopted paper antimacassars. Automobile seat covers are now made in many patterns from coloured woven paper threads in America, and these clean and ornamental covers are being tried out in theatres and cinemas.

Paper curtains are sold at Woolworth's for 79 cents a pair and are used in large numbers. This is largely because the cleaning of textile curtains costs more than 79 cents. They are used until dirty, and are then thrown away. The curtains are flameproofed, and are impregnated with suitable softeners to make them hang well.

In the house, paper bags are now made of suitable air-porosity for use on vacuum cleaners. Here, also, we have paper used for cooking aprons, work gloves, rubbish can liners, hair shields, covers for

garments and for many other purposes, not least interesting being waterproof bath slippers.

One interesting development, which is really a hybrid between textiles and paper, is the so-called "flock" paper, made by applying adhesive in a pattern to paper and then spraying or otherwise applying short-cut rayon fibres. In order to make the fibres stand up, the material may be passed through an electrostatic field and finally dried. It can be used for a number of purposes where textiles formerly served, and is obviously good material for show-case and window decoration.

There are many similarities in working methods. First of all, very close relations exist between the production of paper pulp, bleached or unbleached, and the very similar methods used by textile workers to boil and bleach vegetable fibres. New mechanical and chemical developments worked out by one trade are equally studied and used in the other trade. One has borrowed from the other for processes of impregnation for fire-proofing, insect-proofing, mould- and bacteria-resistance, softening, stiffening, crease-resistance, etc. It might be said here with some truth that chemical processing developed more freely in the textile world and the example was followed by paper. In general the paper trade is more adept with mechanical work and the textile trade with chemical processes.

The paper colourist has taken and adapted to his purpose many dyes produced originally for textiles, although his range of types and processes is more limited in some directions. The textile dyer has more control through his range of working temperatures and the possibilities of aftertreatment, etc. He has probably more difficult problems to face in connection with fading by light, looseness to washing, etc., because, whilst most finished paper is more or less left to its own devices, textiles are subjected to many deleterious agencies during exposure, wear, and laundering.

The mechanical finishes are also very similar in some respects, and particularly as far as calendering is concerned paper is probably much more advanced. Its structure lends itself very well to the production of either very smooth or embossed finishes.

Apart from sound-proofing and the more normal forms of thermal insulation in building, there is an interesting development in which metal-foil-surfaced paper is used as a heat-insulating lining, and it may be found in effective use in such places as constant-temperature testing rooms.

It is very surprising to a textile man that among pulping processes there are practically none in which a precleaning treatment is used comparable with the desizing of textiles. This means that pulping processes tend to be done in one rather brutal operation. It became clear that, if some of the natural impurities of cotton were attacked by such an acid pretreatment, it would greatly help the subsequent alkaline process. In these circumstances it is not so astonishing that, when studying improvements in methods of pulping straw for paper, acid pretreatment of sized textile material came into mind.

Naturally, straw and similar raw materials are very different from cotton, because the latter contains only about 8% of natural impurities, while the former have about 50%.

It was known to us that an acid pretreatment acts especially on the hemicellulose contained in such materials, which amounts to 25–30% of the weight of raw material. This, mainly pentosans, is hydrolysed to sugars and in that way removed from the material. Pentose sugars have many interesting and worthwhile uses, for instance as a basis for the production of such fodder yeasts as *Torula utilis*, and for production of furfuraldehyde or furan products.

Processes based on the same principles had been developed during the war in Germany for the production of rayon pulp by processing pentosan-rich materials like hardwoods, cereal straw, rice straw, etc. In these cases the removal of all pentosans is the main target, regardless of the fact that the fibre is attacked and the chain length of the molecule shortened accordingly. We could not do this, because paper fibre has to keep its strength and other good physical properties. There was a most tiresome and difficult series of trials before we could extract enough pentose sugars with suitable economy, make the treated material much more suitable for a milder alkaline digestion and bleaching process than is normally used, and achieve a satisfactory yield and shade.

This demonstrates an important paper–textile relationship, for the same raw material is treated in the same way for either purpose up to a certain point, the main difference being severity of treatment, and then the desired variation is applied to lead to either paper or rayon.

Fargher, Hart, and Probert[2] have studied the action of acids on cotton fabrics sized in the usual way with starch.

In all cases, textile and paper, it must be strongly emphasised that the fibre must have protection from its coating of impurities. This enables it to withstand a treatment which would have serious consequences on a cleaned and unprotected fibre. According to the conditions of the acid pretreatment, viz. the time, temperature, concentration, and type of acid, more or less of the pentosans may be extracted from the natural fibre.

We have found an increased activity of hydrochloric compared with sulphuric acid in the case or raw pulp materials.

The action of acids on cotton cellulose has been studied also by Birtwell, Clibbens, and Geake[3], Davidson[4], Coward, Wood, and Barrett[5], and Hudson and Waddle[6].

In the German processes for producing rayon pulps, they were forced to achieve a very clean pulp and one particularly freed, as far as possible, from pentosans; otherwise the viscose solution was practically unfilterable. Our object was completely different, namely to produce economically a pulp for paper-making, which has to retain a high quantity of hemicellulose; otherwise the pulp would not hydrate well, and would be unsatisfactory for paper-making. We seem to have been

among the first to suggest this process for the manufacture of paper pulp. There is some evidence that the process would give good results in an economical manner.

Very often the importance of the pH value is overestimated, because the pH is far from being the only important factor, and the individual properties of the acid should not be neglected.

About two years ago we thought that we should use our experience of the acid pretreatment of papermakers' cellulosic raw material for the desizing of cotton goods, since we had learned much about how far we could go without seriously damaging the fibre.

We made some investigations of the aftertreatment of clean alkali-boiled pulp with hot acid, and it was always a failure from the strength point of view until we reduced the temperatures and made the other conditions milder.

Having in mind the low critical temperatures necessary when dealing with the hydrolysis of cellulose within our desired limits, we think we have found a method for an acid aftertreatment of pulp or even, maybe, textiles.

Firstly, we propose to use milder and different acids, and we prefer to use a powder, which can be more easily transported, stored, and handled than strong acids in liquid firm. In this way it more nearly approaches enzyme products, which it may replace. We add to the acid material a detergent. We have had reports of small-scale desizing trials which show that it is effective and has left the fibre strong and sufficiently freed from starch. These tests were very kindly made by the Bleachers' Association Ltd. in their laboratory under the supervision of Mr. F. W. Birch, and he was also good enough to confirm that there was no undesirable degree of damage to our pulp samples which had been pretreated with acid.

Such a powder consists of ten parts of sodium bisulphate and one part of an acid-resistant wetting agent, e.g. Estralene (Stockport United Chemical Co. Ltd.), a sulphated aliphatic alcohol product.

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[4] Davidson, *ibid.*, **34**, T 87 (1943).
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[6] Hudson and Waddle, *Text. Research J.*, **18**, 282 (1948).

Discussion

Mr. F. CROMPTON: In hydrolysing straws with acid, has any use been made of pressure as in the boiling of cotton under pressure?

Dr. ULLMANN: Cooking under pressure damaged the straw and reduced the chain length from about 2000 to 600 glucose units. It is advisable for the temperature to remain below 100°C. for raw straw, and at about 60°C. for alkali-cooked straw, 70°C. being regarded as a critical temperature in the latter case.

Dr. BEAN: In a German rayon process by Jayme either 3% acid was applied at 100°C. or 1% acid at 145°C.

Mr. B. KRAMRISCH: Experiments are also being made with wool flock applied to paper along similar lines to those with rayon flock. The wool has proved to dye very satisfactorily, and it has very good properties as well as being attractive.

Mr. F. A. CRAIG: As a maker of coloured papers I envy the textile industry for the colours they are able to produce, not only in colour range but in fastness to light, acids, alkalis, water, wind, and weather.

Mr. N. HAMER: The protective action of impurities in the materials used for papermaking is exactly the opposite to what applies in textiles.

Dr. ULLMANN: Bleaching cotton is very different from bleaching straw, which will withstand a mild acid process when protected by its impurities, which are considerable and intimately bound to the fibres. The relatively severe chemical treatment which is applied safely to papermaking material is amazing to a textile man.

Mr. R. J. HANNAY: Has any work been done on the application of this type of process to the bleaching of rag and cellulosic materials used for making stronger papers? It would be interesting to know the fluidity number of the final bleached pulp as compared with cotton. If the high-temperature acid process were applied to rag, etc., the result would probably not be the same as with natural straws or pulp.

Dr. BEAN: No experiments have been made with rag materials, as we considered these to be almost completely unprotected, having already been boiled, bleached, worn, etc., and if they were treated further with acid very poor results could be expected. Whilst the acid process is very useful applied to straws, it is not considered practicable for cotton. With fluidity figures of 12–14, satisfactory bursting and tensile strength tests have been made on straw pulps.

Mr. PROVITCH (?): Can stronger materials be produced with a higher fluidity?

Dr. BEAN: Under standard conditions the strength of the paper falls as the fluidity increases, but mechanical effects in papermaking can influence the strength.

Dr. ULLMANN: We have found hydrochloric acid to be much more effective in hydrolysing pulp materials than sulphuric acid.

Mr. HANNAY: There is great scope for an investigation into the use of Dr. Ullmann's hot acid treatment on jute, hemp, linen, and perhaps cotton, although this last offers the least possibilities.

A new method of colouring, in which pigments are bonded to the substrate by means of resins, gives extreme fastness to light, and if the pigment is fixed properly can give a good washing fastness on textiles. No doubt this will be interesting to paper manufacturers who are seeking light-fast colours.

COMMUNICATIONS

The Application of s-Bisalkoxymethylureas (Dialkyl Ethers of Dimethylolurea) to Wool

P. ALEXANDER, D. CARTER, and C. EARLAND

Condensates derived from dialkyl ethers of dimethylolurea have been applied to wool fabric with a view to rendering it unshrinkable. Although the lower ethers are ineffective for this purpose, the condensate from the di-*n*-butyl ether makes fabric unshrinkable with a deposit of less than 10%. Fabric treated with this condensate possesses a greatly improved resistance to abrasion, and yarn an increased tensile strength. It is considered that resins derived from these ethers function by a "spot-welding" mechanism, as do the melamine resins and anhydrocarboxyglycine.

Introduction

1. RENDERING WOOL NON-FELTING WITH RESINS

Wool may be rendered non-felting with resins by building up a film on the surface of the fibres or by internal deposition. Although it has been shown that the shrinkage resistance of wool treated by the latter method is due to the modification of its elastic properties[1], the mechanism of surface deposition is more obscure. It has been stated that the resistance to shrinkage is due to the masking of the scaly surface structure[2], but recently local adhesion or "spot welding" of fibres has also been shown to play an important part[3–5]. Two reasons may be advanced for considering the simple scale-masking theory inadequate. The reduction in the differential frictional effect (D.F.E.) of single fibres after a resin treatment is often insufficient to account for the high degree of shrink-resistance of fabric similarly treated, and local adhesion of fibres occurs in many resin finishes, as is seen from microscopic examination and the increase in tensile strength of treated yarn. The tensile strength of yarn depends on the failure of the yarn to draft, as well as on the strength of the individual fibres.

Among the many resins which have been applied to wool fabric, condensates derived from amines or amides and formaldehyde have figured prominently. Urea–formaldehyde resins which firmly adhere to the wool can be applied by heating the wool with the monomer prior to the addition of the polymerisation catalyst[5,6]. It is probable that the melamine–formaldehyde process[7,8] is the only resin anti-shrink treatment used on a large scale.

Contrary to earlier reports, there is no evidence to show that any resin can be chemically anchored to the surface of wool via its reactive side-chains[5].

A silicone polymer is initially anchored via –Si·NH– linkages to wool by treatment with an organosilicon halide in a solvent, but on milling this bond immediately undergoes hydrolytic fission[9].

2. s-BISALKOXYMETHYLUREAS (ALKYL ETHERS OF DIMETHYLOLUREA)

In view of the successful application of urea–formaldehyde resins as anti-shrink agents for wool[6], the treatment of wool with condensates derived from alkyl ethers of dimethylolurea was investigated.

It has been claimed that *s*-bisalkoxymethylureas produce less tendering than urea–formaldehyde condensates and are more satisfactory for polymerising on to textile materials[10].

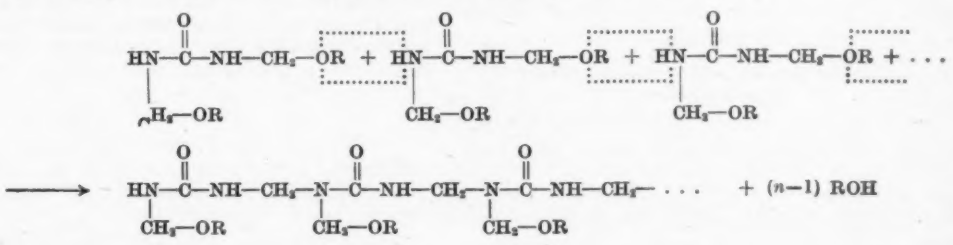
s-Bishydroxymethylurea (dimethylolurea) is prepared by reaction of one molecule of urea with two molecules of formaldehyde, under rigorously controlled conditions to prevent the formation of a urea–formaldehyde condensate—

$$CO(NH_2)_2 + 2\,CH_2O = CO(NH{\cdot}CH_2OH)_2$$

The bishydroxymethylurea is then alkylated by heating with an excess of the corresponding alcohol—

$$CO(NH{\cdot}CH_2OH)_2 + 2\,ROH = CO(NH{\cdot}CH_2{\cdot}O{\cdot}R)_2 + 2\,H_2O$$

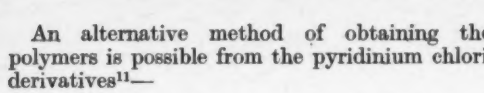
Although the mechanism of condensation of these compounds has not been studied in detail, it is reasonable to assume that their condensation is similar to that of bishydroxymethylurea itself, which first condenses to give a long chain structure and then cross-links. Thus the linear polymer would be produced as follows—



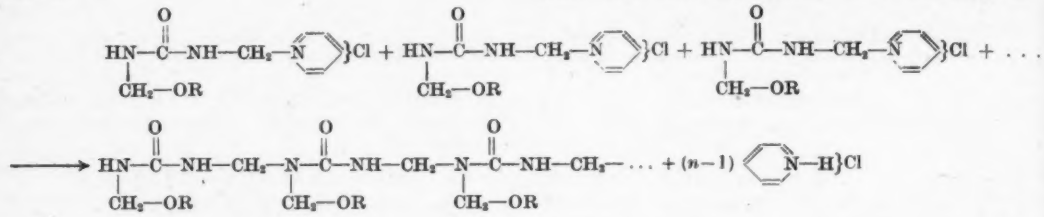
The remaining alkoxy groups then further condense with –NH– groups to produce chain branching.

Although the nitrogen content of the actual resins (Table IX) corresponds approximately to the straight-chain formula shown here, their insolubility in all solvents suggests that they are cross-linked. The actual constitution of the polymers is, therefore, still obscure.

An alternative method of obtaining these polymers is possible from the pyridinium chloride derivatives[11]—



The quaternary salt condenses on heating, as shown below—



These quaternary salts are soluble in water and enable the condensate to be deposited from aqueous solution; whereas the higher alkyl ethers are soluble only in organic solvents such as alcohols.

Experimental

1. MATERIALS

(a) s-Bishydroxymethylurea (Dimethylolurea)

Although the condensation of urea and formaldehyde to bishydroxymethylurea can be carried out in aqueous medium[12], difficulty was found in stopping the condensation at the bishydroxymethylurea stage before polymerisation to a urea–formaldehyde resin occurred. The reaction was easier to control in ethyl alcohol, using sodium hydroxide as condensing agent, since the decreased ionisation of the alkali leads to the formation of bishydroxymethylurea without subsequent polymerisation[13].

Paraformaldehyde (60 g.) and sodium hydroxide (1·5 g.) were dissolved in 94% ethyl alcohol (330 ml.), and a small residue was filtered off. Urea (60 g.) was then dissolved in the cold solution; after 2·5 hr. at room temperature the bishydroxymethylurea began to crystallise out, and after 4 hr. condensation was complete. The bishydroxymethylurea was filtered off, washed with ether, and air-dried. The yield was nearly theoretical. (Found 21·8% N; calc. for $C_3H_8O_3N_2$ 23·3% N.)

(b) Bisalkoxymethylureas (Dialkyl Ethers of Dimethylolurea)

In all cases the bishydroxymethylurea was used within 24 hr. of its preparation. The slight alkalinity of bishydroxymethylurea, inherent in the preparation as described, was neutralised by the addition of oxalic acid to the alkylating solution.

Bishydroxymethylurea (10 g.) was dissolved in the alcohol (50 ml.), and anhydrous magnesium sulphate (5 g.) was added. The reaction mixture was heated for one hour at 80°c. under reflux with stirring. After filtering from magnesium sulphate, a clear solution of the bisalkoxymethylurea in the corresponding alcohol was obtained. When it was desired to isolate the ether, the solvent was removed under vacuum at 40°c. In this way the following dialkyl ethers of dimethylolurea were obtained—methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*-butyl, and *n*-amyl. To prepare the *sec.*-butyl ether the reaction mixture was heated for only 15 min., since further heating caused polymerisation. The *n*-nonyl ether was prepared by using twice the quantity of alcohol stated. The di-*tert.*-butyl ether of dimethylolurea cannot be prepared in this way, and all attempts to make bishydroxymethylurea react with *tert.*-butyl alcohol were unsuccessful.

(c) N-(n-Butoxymethylureidomethyl)pyridinium chloride

Bis-*n*-butoxymethylurea (20 g.), pyridine hydrochloride (12 g.), and ethyl alcohol (30 ml.) were heated under reflux for 30 min. at 70°c. On pouring the clear solution into acetone (400 ml.), the quaternary salt was precipitated as a white solid, which was filtered off, washed with acetone, and dried.

The salt was readily soluble in cold water, and on heating the aqueous solution for 30 min. at 100°c. a white solid was precipitated.

(d) Wool

The wool used was a two-fold 18s yarn of 56/58s quality knitted into fabric using 12 needles and 18 courses per inch. After scouring, the fabric was cut into 5-in. squares. These patterns had a dry weight of approx. 5 g.

2. APPLICATION OF THE RESINS

The patterns of fabric were immersed in a solution of the bisalkoxymethylurea in the corresponding alcohol and then passed through squeeze rollers. The nip was adjusted so that the quantity of solution picked up by the fabric being 100%, i.e. the amount of resin deposited was approximately equal to the quantity of ether in the solution. The pattern was then dried in an oven at 110°c. and heated for a further hour at that temperature.

3. SHRINKAGE TESTING

All shrinkage testing was done by vigorous hand-milling in 1% soap solution at 30°c., the area of the pattern being measured before and after milling. An untreated control pattern was always milled together with the treated pattern. Before determining the area prior to milling, all patterns were allowed to recover from mechanical stresses, i.e. to relax, by immersion for one hour in soap solution.

4. DETERMINATION OF WEIGHT INCREASE DUE TO RESIN DEPOSITION

The treated patterns after drying were placed in a stoppered bottle to cool in a desiccator, and

weighed on an analytical balance. The condensate deposited on the wool was firmly held, and none was removed by washing or a light scour; consequently the patterns were not rinsed prior to weighing. Before the determination of weight increases after milling, the patterns were rinsed for several hours with water.

Results

1. TREATMENT WITH VARIOUS BISALKOXYMETHYLUREAS

The hand-milling shrinkages of patterns after treatment with different ethers are shown in Table I.

TABLE I

Treatment with Various Bisalkoxymethylureas $CO(NH{\cdot}CH_2{\cdot}O{\cdot}Alk)_2$ dissolved in the corresponding Alcohol AlkOH

Alkyl	Resin deposited (%) Before Milling	Resin deposited (%) After Milling	Area Shrinkage (%) Treated	Area Shrinkage (%) Untreated
Methyl	29·1	5·8	19·0	25·2
	28·6	4·9	19·5	25·2
	15·3	9·3	17·3	20·0
	15·3	9·4	25·5	24·7
Ethyl	15·8	8·2	22·6	24·2
	16·8	6·8	30·1	23·2
	~20	—	34·0	31·4
n-Propyl... ...	16·3	2·9	21·8	24·2
	17·2	2·3	24·1	23·2
	~20	—	32·7	31·4
*iso*Propyl ...	16·2	2·9	21·4	24·2
	17·9	1·6	26·4	23·2
	~20	—	36·1	31·4
n-Butyl ...	33·8	25·5	−0·6	21·4
	27·9	24·0	6·0	21·4
	14·2	11·0	3·5	23·7
	12·2	9·0	3·6	24·6
	11·4	9·9	6·0	24·7
	10·8	9·5	3·2	20·0
	7·0	5·2	8·0	17·2
	6·6	5·3	6·4	15·3
sec.-Butyl ...	14·4	13·5	8·5	31·3
	14·3	13·0	5·7	31·3
*iso*Butyl ...	18·9	15·9	14·6	27·7
	17·8	14·7	11·7	27·7
n-Amyl	11·3	10·6	3·8	20·0
	11·4	10·5	2·5	20·0
n-Nonyl	21·1	11·9	10·0	29·0
	18·4	11·1	13·6	29·0
	7·9	5·6	16·7	21·8
	7·0	4·8	16·1	21·8

2. MINIMUM DEPOSIT OF CONDENSATE TO PRODUCE UNSHRINKABILITY

It has been shown in Table I that bis-*n*-butoxymethylurea is the most effective ether for rendering wool fabric unshrinkable. Different weights of this ether were deposited on to fabric, and after drying at 110°C. the hand-milling shrinkages were determined (Table II).

TABLE II

Application of Different Amounts of the Di-*n*-butyl Ether

Resin deposited (%)	Area Shrinkage (%) Treated	Area Shrinkage (%) Untreated
5·1	25·2	37·0
7·6	15·4	37·0
8·7	7·9	25·6
8·9	4·4	37·0
12·5	5·8	37·0
15·7	7·1	25·6
18·8	6·9	37·0
23·4	2·6	25·6
30·3	1·5	25·6

It is thus seen that the minimum deposit necessary to confer resistance to milling shrinkage on fabric is 9%.

3. MINIMUM DRYING TEMPERATURE

In Table III are shown the hand-milling shrinkages of patterns of fabric which were treated with 10% of the di-*n*-butyl ether and dried at different temperatures. In all cases the fabric was heated for an additional hour after it felt dry to the hand.

TABLE III

Effect of Drying Temperature

Drying Temperature (°C.)	Area Shrinkage (%) Treated	Area Shrinkage (%) Untreated
60	17·5	25·2
70	16·2	23·4
	13·9	25·2
80	7·7	24·8
	7·5	24·8
110	6·4	23·4
	6·7	24·8
	6·0	24·8
	4·7	32·5
140	0·3	32·5

The minimum effective drying temperature is therefore 80°C.

One explanation why the lower alkyl ethers of dimethylolurea are ineffective for rendering wool non-felting is that, if they possessed greater stability than the *n*-butyl ether, they would require a higher temperature for polymerisation. Heating wool at 140°C. after treatment with the lower ethers, however, did not increase its resistance to felting (Table IV).

TABLE IV

Application of Lower Ethers with Drying at 140°C.

Ether	Drying Temp. (°C.)	Area Shrinkage (%)
Untreated ...	—	32·2
20% Ethyl ...	140	25·7
20% *n*-Propyl ...	140	26·7
20% *iso*Propyl ...	140	26·8
10% *n*-Butyl ...	110	6·4

4. APPLICATION OF *N*-(*n*-BUTOXYMETHYLUREIDOMETHYL)PYRIDINIUM CHLORIDE

Five-gram patterns of wool fabric were treated as follows—

(*a*) Padded through an 8·5% aqueous solution of the pyridinium salt and dried at 110°C.

(*b*) As (*a*) but using a 24% solution.

(*c*) The pattern was sewn on to a stirrer, treated with 80 ml. of an 8·5% aqueous solution of the pyridinium salt for 30 min. at 100°C., and dried at 110°C.

The figures shown in Table V establish the fact that the polymer deposit obtained via the pyridinium salt does not prevent felting.

TABLE V

Application of *N*-(*n*-Butoxymethylureidomethyl)pyridinium Chloride

Treatment	Resin deposited (%) Before Milling	Resin deposited (%) After Milling	Area Shrinkage (%) Treated	Area Shrinkage (%) Untreated
(*a*)	—	—	24·8	22·3
(*b*)	15·7	9·7	22·2	26·9
	16·3	9·5	25·8	26·9
(*c*)	18·4	10·1	15·4	26·3

5. PROPERTIES OF WOOL TREATED WITH BIS-*n*-BUTOXYMETHYLUREA

(*a*) *Abrasion Resistance of Treated Fabric*

In Table VI are shown the numbers of revolutions required to wear a hole in treated fabric after

it had been impregnated with a pH 7 buffer solution, when tested on the Tootal Broadhurst Lee ring wear tester[14].

TABLE VI

Wet Abrasion of Fabric

Condensate deposited (%)	Revolutions for Wear (mean of 10 results)
0	2,620
8·4	6,520
13·2	10,300

(*b*) *Tensile Strength of Treated Yarn*

The tensile strengths of yarns treated with 10% of the *n*-butyl ether from *n*-butyl alcohol and 10% of the methyl ether from methyl alcohol are given in Table VII. After treatment the yarns were conditioned at 65% R.H. and 20°C.

TABLE VII

Tensile Strength of Yarn

Ether	Breaking Load (oz.) (mean of 20 results) Treated	Untreated
n-Butyl ...	20·0	12·4*
Methyl ...	9·1	7·4*

* The untreated yarns were different in the two experiments

6. THE EFFECT OF THE SOLVENT

In all previous treatments the dialkyl ethers of dimethylolurea were applied from a solution in their corresponding alcohols. The felting resistance imparted by the resin is shown in Table VIII to be independent of the solvent employed; thus the *n*-butyl ether is completely effective from methyl alcohol, and the methyl ether remains ineffective even when applied from *n*-butyl alcohol.

TABLE VIII

Effect of the Solvent

Ether	Solvent Alcohol	Resin deposited before milling (%)	Area Shrinkage (%) Treated	Untreated
Methyl	Methyl	28·6	19·5	25·2
Methyl	*n*-Butyl	20·0	27·1	25·7
n-Butyl	*n*-Butyl	27·9	6·0	21·4
n-Butyl	Methyl	19·9	10·8	33·3

If during the isolation of the *n*-butyl ether the temperature was allowed to exceed 40°C., a partial polymerisation of the ether took place and the material, though still soluble, was ineffective in rendering wool unshrinkable.

7. NATURE OF THE CONDENSATES

It has been shown that the effectiveness of bis-*n*-butoxymethylurea compared with the lower alkyl ethers for rendering wool fabric resistant to milling shrinkage was not due to the different solvents used in their application nor to the different curing temperatures necessary to effect condensation. The difference must lie in the nature of the polymers produced.

The difference between the polymers obtained by heating an aqueous solution of *N*-(*n*-butoxymethylureidomethyl)pyridinium chloride or by evaporating alcoholic solutions of the dimethyl ether or the di-*n*-butyl ether and then heating to 110°C. was at once obvious. The first produced a white powdery product, while the latter two gave tough, clear films of similar mechanical properties. It is, however, seen from Table IX that the polymers obtained from the two ethers were not chemically identical, since their nitrogen contents were different.

TABLE IX

Nitrogen Contents of Condensates

(%)

Polymer from the dimethyl ether	24·1
Theoretical for $[N(CH_2{\cdot}O{\cdot}CH_3){\cdot}CO{\cdot}NH{\cdot}CH_2]_n$	24·1
Polymer from the di-*n*-butyl ether	20·2
Theoretical for $[N(CH_2{\cdot}O{\cdot}C_4H_9){\cdot}CO{\cdot}NH{\cdot}CH_2]_n$ ...	17·7

Discussion

Microscopic examination of material treated with the bis-*n*-butoxymethylurea shows abundant evidence of the bonding of fibres together by the polymer, the photomicrographs obtained being very similar to those for other resin anti-shrink processes which function by the "spot-welding" mechanism[5]. No indication of fibre bonding could be seen in yarns treated with the methyl ether, which fails to give an unshrinkable finish. Reliable determinations of the D.F.E. of fibres treated with bisalkoxymethylureas could not be made since the results were highly irreproducible, probably because the non-uniform local adhesion of resin forms lumps along the fibres. There is no microscopic evidence for uniform scale masking similar to that observed with silicone treatments[5], and it seems unlikely that any reduction of D.F.E. due to scale masking plays a prominent part in the mechanism by which bisalkoxymethylureas prevent felting. Since these resins are applied from non-swelling solvents, they cannot modify the elastic properties of the individual fibres, and they must therefore function by the "spot-welding" mechanism like the melamine resins and anhydrocarboxyglycine[5]. The presence of "spot-welding" in treatments with the *n*-butyl ethers is further proved by the increase in tensile strength of yarn (Table VII) and in the related property of abrasion resistance (Table VI). The tensile strength of yarn is not improved by the deposition of an equal quantity of resin from the methyl ether.

The reason for the ineffectiveness of the lower ethers of dimethylolurea cannot lie in their mechanical properties, since both the methyl and the *n*-butyl ether condense under the same conditions to give flexible resins of considerable mechanical strength, which appear suitable for bonding fibres. It has, however, been pointed out[5] that a material suitable for bonding fibres by bridge adhesion, besides having suitable mechanical properties, must also be capable of forming a firm link with the fibre, and it is probable that it is in this respect that the bisalkoxymethylurea resins differ. This conclusion is supported by the fact that the resins which give unshrinkability are permanent, whereas the others are removed by mechanical action on milling in soap. It was shown in Table IX that the polymers from the methyl and *n*-butyl ethers were of different chemical composition, but no evidence for the molecular constitution of either condensate is available, and no explanation can be suggested why the lower ethers give resins which fail to adhere to wool. It is not possible to find out whether the effective resins form an actual chemical bond or whether they are held to the wool by physical forces only, since no suitable solvents for

these polymers could be found and hence no extraction experiments could be carried out.

The most suitable compound from a practical point of view appears to be the *n*-butyl ether, since it is readily prepared and should be relatively inexpensive. The ether need not be isolated, but can be applied direct from the solution in *n*-butyl alcohol in which it is synthesised. The handle of the treated material, though detectably different from that of untreated fabric, is not unpleasant, and in many ways resembles that of wool treated with anhydrocarboxyglycine. The monomer is easily applied by padding, and no special curing equipment is required, since condensation to the resin takes place at temperatures attainable in ordinary drying equipment.

In our hands only two other resin processes have been found to give as high a degree of unshrinkability to knitted wool fabric as the bis-*n*-butoxymethylurea, with a polymer deposit of less than 10%. These processes employ anhydrocarboxyglycine[3] or silicones[9], and both are very expensive and difficult to apply. Moreover, the very great increase in abrasion resistance is equalled only by the anhydrocarboxyglycine process, and no other resin treatment which we have examined gives a comparable improvement.

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The Action of Chlorine Dioxide on Wool*

D. B. DAS and J. B. SPEAKMAN

When wool is treated with a 1·25 N. solution of chlorine dioxide in the dark at 22°C., there is a rapid fall in cystine content, about a quarter of the sulphur in the wool being oxidised ultimately to sulphuric acid and the remainder to cysteic acid. The reaction appears to be complete in 120 hr., and as much as 40% of the protein is dissolved during treatment and washing. When the treated wool is afterwards boiled in water for 1 hr., the total loss in weight is raised to 87%.

Hydrolysates of wool treated with chlorine dioxide for 120 hr. have been examined by paper chromatography, using phenol–water and collidine–water systems. A large amount of cysteic acid was detected, but no cystine and little, if any, tyrosine. The aspartic acid content, on the other hand, was greater than that of untreated wool. Since Schmidt and Braunsdorf have shown that simple peptides are not attacked by chlorine dioxide, and since wool treated with chlorine dioxide is so readily soluble, even in hot water, it should be possible to determine the average molecular weight of the polypeptide chains of wool keratin by determining the osmotic pressure of solutions of the treated wool in a suitable solvent. The results of such determinations will form the subject of a later paper.

During the course of the investigation it was noticed that the regain of chlorine dioxide-treated wool was invariably less than that of untreated wool. The observation was confirmed by determining the adsorption and desorption isotherms of wools treated with chlorine dioxide for various times, and, since wool containing sulphuric acid has a reduced water-adsorption capacity (at humidities below saturation), it seems probable that the phenomenon must be referred to intimate linking of cysteic acid and arginine side-chains, possibly with hydrogen bonding.

Schmidt and Braunsdorf[1] have shown that most amino acids and simple peptides, such as leucylglycine and triglycine, are not attacked by chlorine dioxide. The exceptions among those examined were tyrosine, tryptophan, histidine, and cystine. Of these, cystine was oxidised to cysteic acid and the remainder to unknown end-products. When, therefore, wool is treated with chlorine dioxide, breakdown of the cystine bonds between the main peptide chains should give a product soluble in the usual protein solvents, and if the main peptide chains remain intact during oxidation and dissolution, their average molecular weight should be capable of determination by osmotic pressure measurements. As a basis for such measurements, it seemed desirable to establish the nature of the reaction between chlorine dioxide and wool—in particular, between chlorine dioxide and the cystine cross-linkages—and the conditions under which reaction is complete.

Experimental

PREPARATION OF MATERIALS

(*a*) WOOL—Except where otherwise stated, Lincoln wool was used throughout the following experiments. The root ends of staples taken from the back of a single fleece were purified by extraction with alcohol and ether in a Soxhlet apparatus, followed by washing in water. After the wool had been dried, it was freed from vegetable matter and coloured wool by hand, any traces of grease absorbed in the process being afterwards removed by further extraction with alcohol and ether. The wool was then rinsed in distilled water and transferred to a 0·001 N. solution of hydrochloric acid to minimise the ash content. Acid was added at

* Part of a lecture to the West Riding Section of the Society on 31st January 1950, Mr. E. A. SWIFT in the chair.

intervals, and after the pH of the solution had been found to remain at 3·15 over a period of 6 hr., the wool was washed in distilled water until free from chloride. It was then centrifuged, dried in air, cut into 1-cm. lengths, mixed thoroughly, and stored in a room at 22·2°C. over a solution of sulphuric acid at 70% R.H. The ash content of the wool, determined by igniting samples of known dry weight (1 g.) in a platinum crucible, was 0·1%.

In order to characterise the wool, total sulphur was determined by the Carius method, cystine and cysteine by a simple modification of Shinohara's method[2], and methionine by Baernstein's procedure[3]. The results are given in Table I.

TABLE I
(% on dry weight)

Total sulphur	3·34
Cystine	9·9
Cysteine	0·55
Methionine	0·80

(*b*) CHLORINE DIOXIDE was prepared according to the method of Schmidt and Graumann[4] by heating an intimate mixture of potassium chlorate and oxalic acid with sulphuric acid for 6 hr. at 40°C. and 1 hr. at 60°C. The gas was bubbled through two wash-bottles containing a 10% solution of silver nitrate before being absorbed in water. In order to prevent decomposition of the reagent, it was prepared in the dark, and on testing the aqueous solution with silver nitrate it was found to be free from chlorine.

A fresh solution of chlorine dioxide was prepared for each set of experiments, and its concentration was determined in the following manner. The chlorine dioxide solution (2 c.c.) was pipetted into a flask containing a 10% solution of sulphuric acid (5 c.c.) and water (50 c.c.). Solid potassium iodide (3 g.) was added and, after 5 min., the whole was diluted to 200 c.c. The iodine liberated according to the following equation—

$$2\,ClO_2 + 10\,KI + 4\,H_2SO_4 = 2\,KCl + 5\,I_2 + 4\,H_2O + 4\,K_2SO_4$$

was then titrated with 0·1 N. sodium thiosulphate solution.

CONDITIONS OF TREATMENT

As chlorine dioxide undergoes slow decomposition into its elements during exposure to light, the wool was always treated with the reagent in the dark in order to avoid complications due to the independent action of chlorine on wool. In addition, dilute aqueous solutions of chlorine dioxide were used so as to prevent hydrolysis of the main peptide chains by the hydrochloric acid and, as will be seen later, the sulphuric acid which are formed during the reaction with wool. A typical procedure was as follows— An amount of conditioned wool corresponding to a dry weight of about 3 g. was weighed out in a weighing bottle and then transferred quantitatively to a 150-c.c. standard-joint flask. Freshly prepared chlorine dioxide solution (150 c.c., 1·25 N.) was then added and, after shaking to ensure complete wetting-out of the wool, the flask was closed with a ground-glass stopper and kept in a water thermostat at 22 ± 0·1°C. for the required length of time in a dark room. At the end of this time, the flask was removed and the contents, after filtration through a tared sintered glass crucible, were washed with several changes of distilled water. In order to ensure complete removal of chlorine dioxide, hydrochloric acid, and sulphuric acid, the wool was removed, immersed in distilled water for 1 hr., and filtered again under suction. Seven such washings were given each day for 2–3 days until the filtrate was free from sulphuric acid, a total of 4 litres of water being used. Finally, the crucible and its contents were stored in an atmosphere at 70% R.H. and 22·2°C. so that the conditioned* weight of the wool could be determined. Whenever necessary, the dry weight of the wool was obtained by drying to constant weight over phosphorus pentoxide *in vacuo* at room temperature.

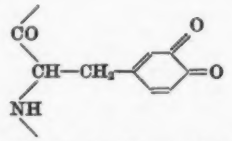
OBSERVATIONS AND RESULTS

(*a*) COLOUR CHANGES— During treatment with chlorine dioxide, wool undergoes an interesting series of colour changes. Observations made in a typical experiment, where the wool was treated with a 1·25 N. solution of chlorine dioxide at 22°C., using a liquor ratio of 50 : 1, are given in Table II.

TABLE II

Time of Treatment (hr.)	Colour of Wool
0 ...	White
1 ...	Deep brown
24 ...	Light brown
72 ...	Yellow
120 ...	Faint yellow
168 ...	White
240 ...	Bleached white

It seems probable that the development of colour during the early stages of treatment is due to oxidation of tyrosine side-chains to the corresponding *o*-quinone—



and further oxidation, leading to the disappearance of colour, is almost complete after 5 days' treatment.

(*b*) CHANGE IN CYSTINE CONTENT— In a first attempt to determine the rate at which the cystine cross-linkages are oxidised by chlorine dioxide, samples of wool were treated with 1·25 N. chlorine dioxide for various times at 22°C., using a liquor ratio of 50 : 1. The treated wools did not contain any appreciable amount of cysteine, and their cystine contents were determined after washing and drying in the manner already described. From the results, which are given in Table III, it is

TABLE III

Time of Treatment (min.)	Cystine Content of Residual Wool (% on dry weight)
0	10·2 (including cysteine)
5	6·7
10	5·4
20	5·2
45	4·0
60	3·5
135	2·7

* Throughout this paper the term "conditioned" implies equilibrium with an atmosphere at 70% R.H. and 22·2°C.

obvious that the cystine cross-linkages are much more rapidly oxidised than tyrosine side-chains, if the latter are responsible for the colour changes already discussed.

(*c*) CHANGE IN SULPHUR CONTENT—If the cystine cross-linkages of wool are oxidised to cysteic acid side-chains by reaction with chlorine dioxide, as would be expected from the behaviour of free cystine, the sulphur content of the fibres should be unchanged after treatment, unless there is preferential dissolution of protein rich in combined cysteic acid. Because of this possible complication, the loss in weight of the wool during chlorine dioxide treatment and washing was determined, as well as the sulphur content of the residual wool, in the following experiments. Samples of known dry weight were treated with 1·25 N. chlorine dioxide for various times under the usual conditions and then washed, dried, and reweighed. The observed changes in weight are given in Table IV, which includes values for the sulphur contents of the residual wools, determined by the Carius method.

TABLE IV

Time of Treatment (hr. min.)	Loss in Weight (% on dry weight)	Sulphur Content of Residual Wool (% on dry weight)
0	0·0	3·34
10	− 0·5	2·81
20	0·2	2·84
30	0·6	2·62
45	2·1	2·59
60	3·6	2·60
24	25·5	1·96
72	33·8	1·58
120	40·8	1·26
144	42·0	1·26
168	42·3	1·28
192	44·9	1·26

Contrary to expectation, the sulphur content of the wool falls with increasing time of treatment, even during the first hour, when the loss in weight is small. Although part of the sulphur must, therefore, be oxidised to sulphuric acid, the fact that the fall in cystine content (Table III) is so much more rapid than the fall in sulphur content during the first hour of treatment suggests that a large part of the combined cystine is oxidised to combined cysteic acid. Since the sulphur content of the residual wool undergoes no further change after 120 hr. treatment, it may be concluded that the reaction between chlorine dioxide and the cystine of wool is complete in that time.

(*d*) DISTRIBUTION OF SULPHUR AMONG THE REACTION PRODUCTS—In order to determine the fate of the sulphur when wool is treated with chlorine dioxide, it was decided to determine the amount of sulphuric acid formed, the sulphur content of the dissolved protein, and that of the residual wool. For these purposes, conditioned wool (5 g.) of known moisture content was treated with 1·25 N. chlorine dioxide solution (250 c.c.) in a stoppered flask for 5 days at 22°C. in the dark. At the end of this time the solution was filtered through a tared sintered glass crucible, and the wool washed well with distilled water. In order to ensure complete removal of sulphuric acid, the wool was afterwards given 7–8 washings per day, each with 40 c.c. of distilled water for 1 hr., over a period of 3 days. The final filtrate was free from sulphuric acid, and after the dry weight of the residual wool had been determined, its sulphur content was estimated by the Carius method.

The combined filtrate and washings, after being freed from chlorine dioxide by passing a stream of nitrogen through the solution at 30°C., were made up to 2 litres with distilled water. A 500-c.c. aliquot was then removed for gravimetric estimation of sulphate in the usual way.

Finally, a second 500-c.c. aliquot was used in determining the total sulphur content of the filtrate and washings by the Benedict–Denis method, the sulphur contained in the dissolved protein being estimated by subtracting the sulphate sulphur from the total.

The results of a typical experiment are given in Table V.

TABLE V

Source of Sulphur	Sulphur Content (mg.)	
Original wool (4·6405 g. dry wt.) ...	155	
Residual wool (2·9874 g. dry wt., 35·6% loss*) ...	38·9	
Sulphuric acid in filtrate	36·6	163·3
Dissolved protein	87·8	

* The loss in weight is less than that recorded in Table IV because less wash-water was used.

Although the sulphur content of the three fractions, taken together, is greater than that of the original wool, the error is not serious; some difficulty was encountered in estimating sulphuric acid in presence of the large amount of dissolved protein, but there can be no doubt that about one-quarter of the total sulphur is oxidised to sulphuric acid. A small part of the latter may be derived from methionine, because it was found that under the usual conditions of treatment the methionine content of the wool was reduced from 0·8 to 0·1% in 1 hr., and to zero in 120 hr., but the bulk of the sulphuric acid must be obtained from cystine or non-disulphide sulphur. While it is tempting to suppose that it comes from one of Phillips'[5] four sub-fractions of cystine, the only evidence in support of the possibility is the one of numerical coincidence.

From the data of Table V it can be shown that the sulphur content of the dissolved protein is 5·3%, whereas that of the residual wool is only 1·3%. If, as seems probable, most of the cystine of wool is oxidised to combined cysteic acid by the action of chlorine dioxide, separation of the protein into soluble and insoluble fractions of high and low sulphur content, respectively, is to be expected.

(*e*) PARTITION CHROMATOGRAPHY—As already mentioned, the data of Table IV suggest that the reaction between chlorine dioxide and the sulphur-containing amino acids in wool is complete in 120 hr. at 22°C. In order to confirm this conclusion and to show that most of the cystine is oxidised to cysteic acid, as well as to discover the fate of other amino acids, wool treated with chlorine dioxide was examined by paper chromatography.

After the wool had been treated for 5 days at 22°C. with 1·25 N. chlorine dioxide, washed, and conditioned, an amount equivalent to 0·120 g. dry weight was weighed out and hydrolysed with 5 c.c. of 6 N. hydrochloric acid for 42 hr. at 135°C. in an

atmosphere of nitrogen. The hydrolysate was filtered through a sintered glass funnel into a 50-c.c. flask, the filtrate and washings being afterwards evaporated to dryness *in vacuo*. Water (15 c.c.) was then added, and the solution again evaporated to dryness, the process of dilution and evaporation being repeated three times. Finally, the residue was dissolved in exactly 2 c.c. of distilled water. For reference purposes, a similar solution was prepared from untreated wool. Both solutions were then examined in the following manner with the help of Dr. R. Consden of the Wool Industries Research Association.

To one corner (6 cm. from either edge) of a sheet of Whatman No. 4 filter paper (24 in. × 18 in.) was added 6·7 μl. (400 μg.) of the hydrolysate of the treated wool by means of a micropipette. One edge of the vertical paper was then immersed in a horizontal trough containing 30 c.c. of collidine saturated with water. The chromatogram was allowed to develop for 48 hr. in air over a mixture of collidine and water, the system being surrounded by a glass chamber. At the end of this time, the paper was removed, dried, and turned through 90°, so that when the edge was immersed in a saturated aqueous solution of phenol the flow was at right-angles to that of the aqueous collidine. The chromatogram was allowed to develop for 17 hr. in an atmosphere of coal gas, the system being enclosed by an inverted metal box; the open end of the latter was sealed by introducing 2 litres of a 0·2% solution of ammonia into the metal tray in which it stood, aqueous ammonia being used in order to regulate the movement of the amino acids. After the paper had been removed and dried in a current of hot air, it was sprayed with a 0·1% solution of ninhydrin in *n*-butanol and again dried. Finally, the paper was heated in an air-oven at 105°c. for 3 min. before being photographed. For reference purposes, the chromatogram of the same amount of the hydrolysate of untreated wool was developed on the same sheet of filter paper, and photographs of both chromatograms are reproduced in Fig. 1 and 2.

Comparison of the two photographs shows that there is no cystine and little, if any, tyrosine in the wool treated with chlorine dioxide, but a considerable amount of cysteic acid. One-dimensional chromatograms, using phenol–water and collidine–water separately, suggested that the treated wool contains more aspartic acid, glutamic acid, leucine and its isomers, and probably lysine, alanine, and valine, than untreated wool. On the other hand, the treated wool contains less proline and, perhaps, threonine and phenylalanine, though its glycine, arginine, and serine contents are similar to those of untreated wool. The greater amount of aspartic acid in the treated wool may be due to oxidation of other amino acids such as histidine, methionine, tyrosine, and tryptophan, but no certain conclusion can be drawn because the other observed changes in amino acid content must be attributed to differences in composition of the soluble and insoluble fractions of the treated wool.

In the light of these results, it was decided to treat wool with 1·25 N. chlorine dioxide for 120 hr. at 22°c., using a liquor ratio of 50 : 1, for subsequent determinations of molecular weight.

(*f*) SUPERCONTRACTION— Since disulphide bond breakdown is known to promote supercontraction, it is to be expected that wool fibres will contract during treatment with chlorine dioxide and, especially, during subsequent release in boiling water. These predictions were confirmed in the following experiments.

After determining its original length (about 9 cm.) by means of the Sever instrument[6], the root portion of a Lincoln wool fibre was treated with 20 c.c. of 1·25 N. chlorine dioxide in a stoppered glass tube for the desired time at 22°c. The fibre was then washed in several changes of distilled water, kept in distilled water overnight, dried in complete absence of tension, and conditioned before redetermining its length. Once the change in length during treatment with chlorine dioxide had been determined in this way, a 5-cm. length of the fibre was mounted in a stainless steel setting frame, and its exact length measured with a travelling microscope. The top clamp of the frame was then screwed down so as to slacken the fibre, which was immersed in boiling water for 1 hr. After drying and conditioning, the fibre was again drawn taut and its length redetermined. A summary of the results obtained with fibres treated with chlorine dioxide for various times is given in Table VI.

TABLE VI

Time of Treatment (hr.)	Total Supercontraction (% on original length) After Chlorine Dioxide	After Chlorine Dioxide and Boiling
1	4·6	40·5
	6·3	41·7
24	18·4	52·9
	17·3	50·0
48	19·4	52·5
	19·0	53·9
72	21·9	50·6
	21·5	50·9
96	22·4	49·6
	22·1	50·3
120	23·7	49·0
	24·4	49·2

On comparing these data with those of Table IV, it is obvious that the supercontraction during treatment with chlorine dioxide and subsequent washing is not marked until the loss in weight of the fibres is considerable, i.e. after 1 hr. The increased supercontraction in boiling water may not, therefore, be due solely to increased molecular agitation but to further dissolution of protein. In order to examine this possibility 1-g. samples of chlorine dioxide-treated wool were each boiled for 1 hr. in 500 c.c. of distilled water, and, after being filtered off in a sintered glass crucible, dried and reweighed. The losses in weight due to treatment with chlorine dioxide and boiling are compared with those due to chlorine dioxide treatment alone in Table VII.

TABLE VII

Time of Treatment (hr.)	Total Loss in Weight (% on dry weight) After Chlorine Dioxide	After Chlorine Dioxide and Boiling
1	3·6	26·4
24	25·5	49·3
72	33·8	64·8
120	40·8	86·6

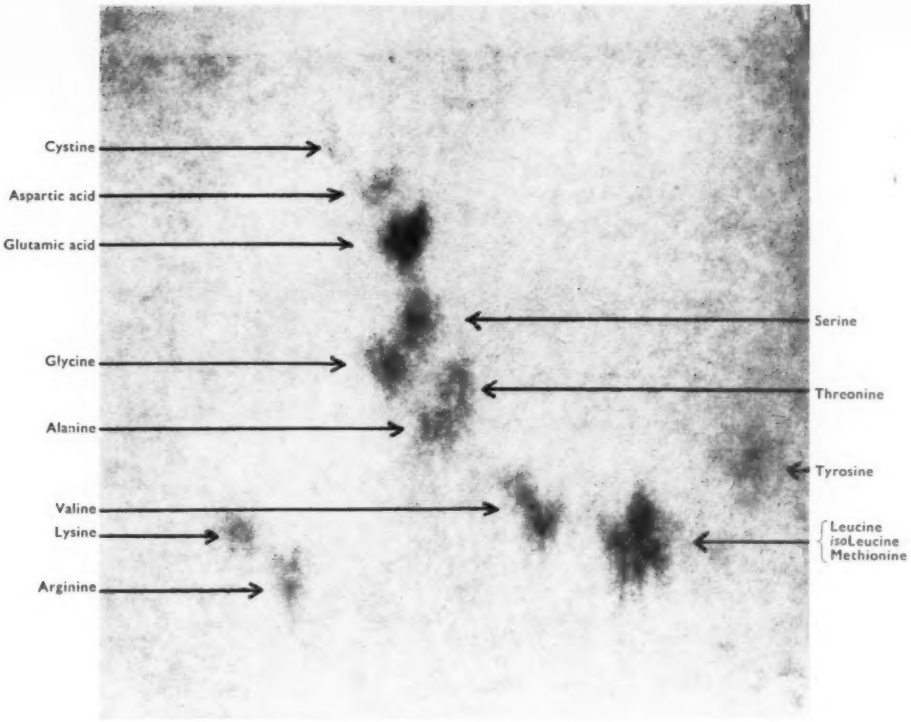


FIG. 1—Chromatogram of Untreated Wool

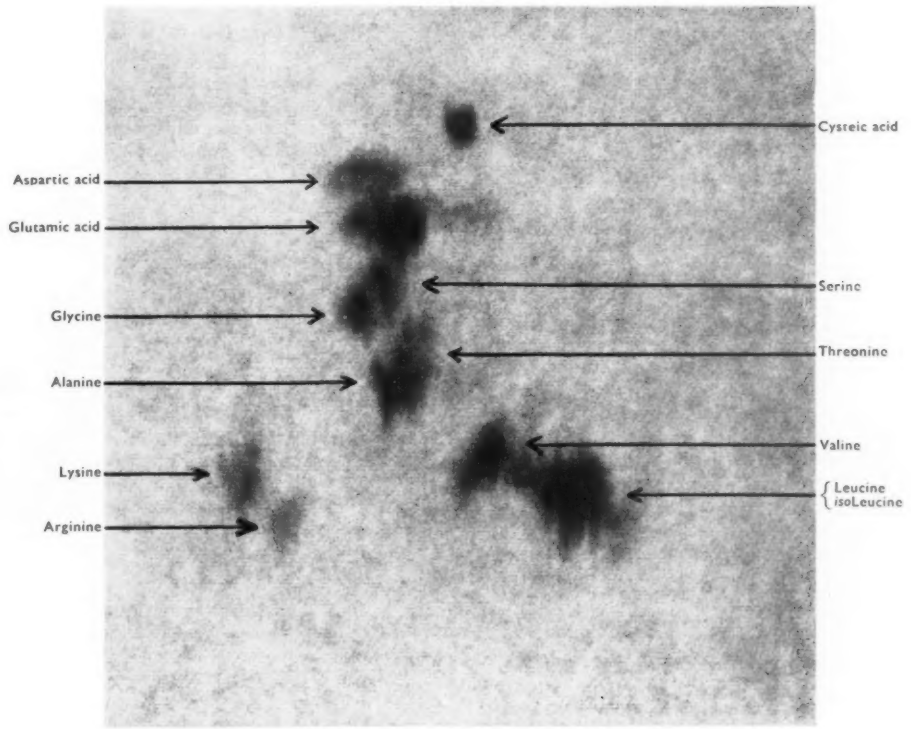
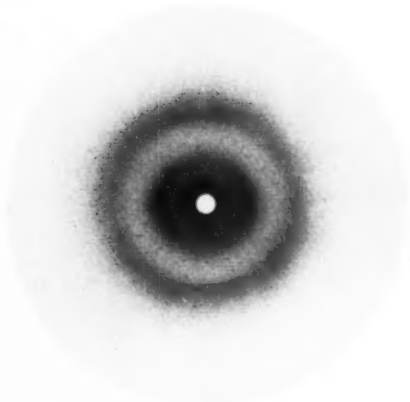
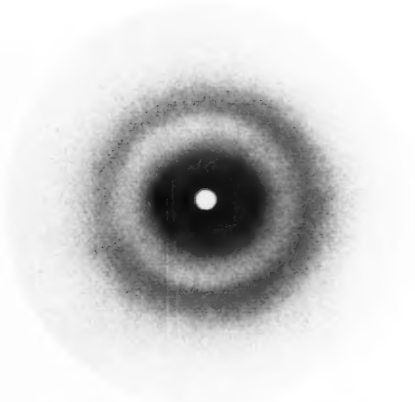


FIG. 2—Chromatogram of Treated Wool



Wool treated with Chlorine Dioxide for 1 day



Wool treated with Chlorine Dioxide for 5 days

FIG. 3

In all cases the loss in weight is greatly increased by boiling, and it is interesting, in connection with the intended use of chlorine dioxide-treated wool for molecular weight determinations, that as much as 86·6% of the protein is soluble in boiling water after treatment with chlorine dioxide for 120 hr. The increased supercontraction of chlorine dioxide-treated fibres in boiling water is not, however, due solely to further dissolution of protein. For example, the loss in weight of fibres after treatment with chlorine dioxide for 24 hr. (25·5%) is almost the same as that of fibres treated for 1 hr. and then boiled in water for 1 hr. (26·4%); but the corresponding degrees of supercontraction are 17·9 and 41·1%. There can be no doubt, therefore, that supercontraction is due, in part at least, to molecular rearrangement which is not dependent on dissolution of protein.

The supercontraction which wool fibres undergo during treatment with chlorine dioxide and subsequent washing should, according to the preceding argument, be accompanied by changes in molecular structure which can be detected by X-ray examination. A bundle of Lincoln wool fibres (0·3 g.) was therefore tied together at one end with cotton thread and treated with 15 c.c. of 1·25 N chlorine dioxide at 22°C. for the desired time. The fibres were then washed in several changes of distilled water, dried, and mounted without tension in a stainless steel frame to give a set of parallel fibres about 1 mm. thick. Four such specimens were prepared from untreated wool and wool treated with chlorine dioxide for 1 hr., 1 day, and 5 days. Their X-ray photographs were taken by Mr. H. J. Woods and Mr. W. J. Onions, using CuK_α radiation, and some of the results are shown in Fig. 3.

The wool treated with chlorine dioxide for 1 hr. shows a disoriented α-photograph, which is usually evidence of some contraction; and, in accordance with the fact that treatment for 1 day causes greater supercontraction (Table VI), the corresponding X-ray photograph shows greater disorientation of the α-structure and some sign of disoriented but poorly crystalline β-keratin. The X-ray photograph of wool treated with chlorine dioxide for 5 days is similar to that of wool treated for 1 day, but the α-keratin is more diffuse and less well oriented, while the β-photograph is stronger and perhaps sharper. In general, the results conform well with the supercontraction measurements.

(*g*) Water Adsorption— Through determinations of the dry weights of conditioned samples of chlorine dioxide-treated wool during the course of this investigation, it was found that the regain fell with increasing time of treatment. Typical results for wools treated with 1·25 N. chlorine dioxide solution at 22°C. for various times, using a liquor ratio of 50 : 1, are given in Table VIII.

As shown in Table IV, there is little loss in weight during the first hour of treatment, and the pronounced fall in regain cannot, therefore, be attributed to preferential dissolution of protein rich in hydrophilic side-chains. Further, since the treated wool contains cysteic acid and is richer in aspartic acid than untreated wool, a rise of regain after treatment with chlorine dioxide might be expected. Because of the surprising nature of the preceding results, adsorption and desorption isotherms were determined with a series of samples by exposing them to sulphuric acid solutions of known R.H. at 22·2°C. after previous drying over phosphorus pentoxide *in vacuo* at the same temperature. The results are collected in Table IX.

Table VIII

Time of Treatment hr.	min.	Regain (%)
	0	17·0
	10	16·1
	20	15·8
	30	14·7
	45	14·6
	60	14·6
24		14·2
72		13·1
120		12·8
144		12·4
168		12·4
192		12·3
240		12·4

Table IX

Relative Humidity (%)	Water adsorbed (% on dry weight) by Wool treated with Chlorine Dioxide for— 0	0·5	24	144 hr.
	Adsorption			
10·0	3·85	3·31	3·28	3·01
25·2	6·76	5·77	5·42	4·96
35·7	8·37	6·99	7·10	6·27
49·0	11·3	9·75	9·35	8·62
65·4	14·8	12·4	11·7	10·9
75·2	17·5	14·3	13·6	12·7
90·4	24·4	20·4	20·8	19·1
100·0	(32·8)	(33·8)	(35·6)	(30·9)
	Desorption			
89·0	25·6	21·3	20·9	19·5
73·5	18·8	15·7	14·4	13·3
63·0	16·5	14·3	13·0	11·8
48·8	13·1	12·0	11·2	9·93
35·0	10·1	9·45	8·95	7·95
7·8	5·09	4·58	4·44	3·79

Even after only 30 min. treatment, the fall in affinity for water is remarkable, and as the corresponding loss in weight is negligible, it seems clear

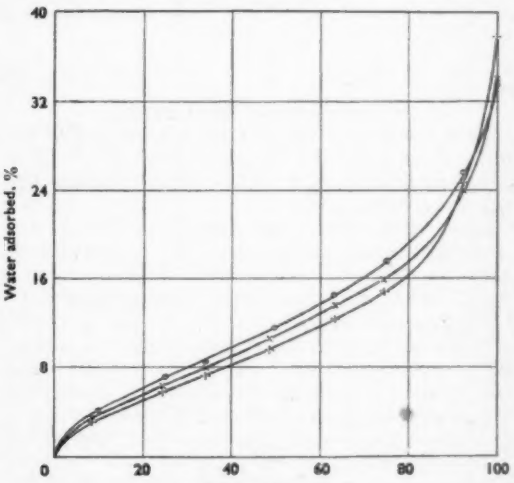


Fig. 4

that the change must be referred to the conversion of cystine cross-linkages into cysteic acid side-chains. Support for this view is provided by the data of Table III, if the rapid fall in cystine content during treatment with chlorine dioxide is due to the formation of cysteic acid side-chains, as well as by the reduced water-adsorption capacity of wool containing sulphuric acid. Adsorption and desorption isotherms for Cotswold wool containing different amounts of sulphuric acid were determined in 1929, and as the results have not yet been published the adsorption isotherms are reproduced in Fig. 4 for comparison with the data for chlorine dioxide-treated wool. As before, the samples were exposed to sulphuric acid solutions of known relative humidity at 25°C.

In view of the hygroscopicity of sulphuric acid, it is strange that the water-adsorption capacity of the wool should decrease with increasing acid content, but the observation lends support to the following interpretation of the similar behaviour of chlorine dioxide-treated wool. There can be little doubt that much of the affinity of untreated wool for water is associated with the salt linkages, of which those containing arginine side-chains form a high proportion. When cysteic acid side-chains are formed by the oxidation of cystine cross-linkages with chlorine dioxide, the carboxylic acid side-chains will be back-titrated by the stronger acid, and if the sulpho groups are closely associated with the arginine side-chains, possibly with hydrogen bonding, the water-adsorption capacity of the protein may well be reduced.

The authors are indebted to the Director of Research of the Wool Industries Research Association for providing facilities for the chromatographic examination of protein hydrolysates, and to Dr. R. Consden for assistance in this section of the investigation.

TEXTILE CHEMISTRY LABORATORY
DEPARTMENT OF TEXTILE INDUSTRIES
THE UNIVERSITY
LEEDS

(*Received 9th June 1950*)

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[6] Sever, *J. Textile Inst.*, **23**, P 151 (1932).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Standardisation of Dyes

The Editor

SIR,

I can assure Mr. Shackleton[1] that from 1906 (when I entered the trade) until 1914 the standardisation of all dyes made by the German and Swiss manufacturers was quite equal to that of to-day. I agree with Dr. Whittaker[1] that there has probably been considerable progress in the *methods* of standardisation.

Yours faithfully

J. KERR MCCALLUM

LAIGHPARK DYEWORKS
PAISLEY

7th September 1950

[1] J.S.D.C., **66**, 375 (July 1950)

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 20th September 1950, the proceedings included the following items of interest—

ANNUAL CONGRESS OF THE A.C.I.T.— It was reported that the Society had been represented at Lille by Messrs. H. Blackshaw, J. Boulton, and E. A. Swift, who had been warmly welcomed by their French colleagues.

SUMMER SCHOOL IN LEEDS— The Honorary Secretary reported that this Summer School, run in conjunction with the University of Leeds, had been highly successful. The cordial appreciation of Council was expressed to those who had contributed to the success of the School.

REPORT OF THE VAT DYES COMMITTEE—The Report of the Committee on the Dyeing Properties of Vat Dyes was approved, and it was resolved that the members be informed of the appreciation and gratitude of Council for their valuable work.

LONDON SECTION BYE-LAWS— Draft bye-laws of the London Section were approved.

MEMBERSHIP — Twenty-six applications for ordinary membership and one for junior membership were approved. Messrs. H. Köhler and C. Subramaniam were readmitted to membership.

Deaths of Members

We regret to report the loss of Professor W. R. Atkin, Mr. H. Downs, and Mr. E. F. North.

Meetings of Council and Committees
October

Council— 11th
Finance— 11th
Publications— 17th
Fastness Tests Co-ordinating— 12th
Historical Records— 2nd
Conference— 2nd
Mercer Lecture— 6th
Dyers' Company's Medal— 17th

Scottish Section
Report for the Session 1949-1950

The Committee has pleasure in again reporting a happy and successful session. Eight meetings were held during the period under review, and the Committee has tried to make these as varied and interesting as possible. Attendances at lectures have been very good.

During the session we enrolled 21 new members, but owing to transfers to other districts, etc., our net gain is only 10, our total membership now being 216.

Mr. E. D. Kennedy retires from the Chairmanship after two years of office, and we take this opportunity of expressing our appreciation of his work for the Section.

The following officers have been nominated by the Committee for the ensuing period—

Chairman	D. B. F. McAndrew
Vice-chairman ...	R. D. Alexander
Honorary Secretary ...	F. Atack

F. Atack
Honorary Secretary, Scottish Section

B.S.I. Manchester Branch Office

The British Standards Institution has opened a branch office at 12 Hilton Street, Manchester 1 (telephone: CENtral 4856; telegrams: Bristandin, Manchester). At this office a complete set of British Standards, some 1600 in number, may be consulted and copies purchased if desired.

Any information about the B.S.I. can be obtained from Mr. A. F. B. Nall, an Assistant Technical Director of the Institution, who is in charge of the Manchester office.

OBITUARY NOTICE

Thomas Frederick Gorton

We regret to record the death on 9th June 1950 of Thomas Frederick Gorton, at the age of 56. He was born at Chorlton-cum-Hardy, where he spent the greater part of his early years, and was educated at Manchester Grammar School and the Royal Technical College, Salford.

His first industrial appointment was with R. P. Lawson & Sons Ltd., yarn dyers and mercerisers, of Manchester, where he gained laboratory and practical experience under the guidance of our President, Mr. F. Scholefield. In 1920 he became technical and sales representative, chiefly in the Leicester district, for Norman Evans & Rais Ltd., chemical manufacturers and at that time agents for Kalle & Co. In 1931 he joined the Geigy Colour Co. Ltd., now the Geigy Co. Ltd. As sales manager for textile auxiliary products he covered the United Kingdom and made many trips abroad. He served with the Special Brigade R.E. in the first World War and was an enthusiastic member of the Royal Observer Corps during the second.

Although he was a member of the Society for many years and a regular attender at meetings, he took no active part in the Society's affairs until the formation of the Mothproofing Committee in 1948. His commercial and technical experience made him particularly well fitted to serve on this committee.

Tom Gorton was notable for his remarkable capacity for making friends, regardless of nationality, and his infectious enthusiasm for any cause that he deemed right. In his youth he was a keen lacrosse player; in later years he turned to golf, being elected captain of the Chapel-en-le-Frith Golf Club in his 55th year. He possessed a pleasing tenor voice, and took an active part in local operatic and dramatic productions throughout his life. He was also well known as a breeder of black-coated retrievers.

His loss will be mourned by a wide circle of friends. F. L. Goodall

New Books and Publications

Mothproofing

By R. W. Moncrieff. 1950. Pp. xiv + 186. London: Leonard Hill Ltd. Price, 17s. 0d.

During recent years increasing attention has been given by scientists and manufacturers to the problem of mothproofing. The general public, on the other hand, appears to be unaware of the developments which have taken place, and the publication of this book should do much to remedy this deficiency.

The book, which covers, if not exhaustively, many aspects of mothproofing, is written in a lively and lucid style, and should prove very interesting to the layman. To scientific workers engaged in work on the subject, the book may be of less interest, as it is based, not so much on first-hand knowledge, as on a patient study of the literature.

Chapters I–III are devoted to a description of a number of clothes moths and carpet beetles, their habits, and the nature of the damage they cause, whilst Chapter XII, which the reviewer thinks should logically follow Chapter III, discusses the nutritional requirements of clothes moths. These parts of the book are, perhaps, the least satisfactory, an oversimplified picture of the habits of the insects being drawn, giving the impression that little more is to be discovered about them. In fact, whilst much has been learned, much remains to be discovered. One important omission in Chapter XII is a reference to the work of Fraenkel and Blewett, who, in addition to showing that a sterol is essential for growth, also studied the effect of the various substances present in the vitamin B complex on the development of the common clothes moth.

Chapters IV–XI give an account of the historical development, the chemistry, and application of the more important mothproofers. These include—nitrophenols such as Martius Yellow, fluorides, the Eulans based on triphenylmethane, Mitin FF, pentachlorophenol, D.D.T., phosphonium compounds, and formaldehyde. The author is quite at home when describing the chemistry and application of these proofers, but the value of his assessment of their fastness properties is reduced by the fact that it is based on claims made by the proprietors rather than on independent investigations of the products by the author.

In this connection the reviewer and his colleagues are, so to speak, "hoisted with their own petar", for on p. 64, in discussing Eulan N, the following sentence occurs— "According to Hartley, Elsworth and Barritt, the proof is fast to all agencies except severe milling". Owing, perhaps, to the unfortunate phrasing, Mr. Moncrieff's interpretation is justified. Since 1943, when the above was written, the reviewer and his colleagues have carried out further work on the fastness properties of mothproofing compounds. All so far examined are removed on washing, some more rapidly than others, Eulan N and also Eulan CN, Mitin FF, and Lanoc CN being in the group of compounds less readily removed.

Chapter XIII gives an account of the mothproofing of wool by modification of the wool structure. It is a subject in which the author is obviously deeply interested. Ever since Harris and his colleagues demonstrated that wool could be made mothproof by modification of the disulphide bond, there has been much speculation on the possibility of a cheap and easy method of producing a modified wool which is mothproof throughout its life. If the author's reasoning with regard to his glyoxal process is correct, this method would appear to fulfil the necessary requirements. The reviewer, having examined a number of such methods, is inclined to be cautious, and feels that theory may have been allowed to outstrip practice.

The omission of any reference to D.D.T. in Chapter XIV, which describes mothproofing during dry cleaning, is surprising, as the use of this compound is established. In the Chapter on D.D.T. (IX), it is felt that the author has not fully realised the potentialities of the substance. Whilst it is true that under certain conditions D.D.T. is slowly volatile, and possesses poor washing fastness, its effectiveness at very low concentrations tends to outweigh these disadvantages.

Chapter XV, entitled "Infestation Precautions and Remedies" is excellent, and should prove very useful to the housewife.

The introduction to Chapter XVI, in which testing methods are described, will be of particular interest to those engaged in this work. The author wonders if all the refinements in test methods which are being put forward are really necessary. Larval testing, which involves the use of living subjects, is full of pitfalls, and the refinements in method have arisen in attempts to obtain consistent results.

The section on chemical methods of test could with advantage be enlarged, as such methods are much quicker than larval testing and more suitable for works control.

The book appears to be unusually free from typographical errors, but on page 25, Fig. 1B, "The Black Carpet Beetle, *Attagenus pellio*" should read "Furriers' Beetle, *Attagenus pellio*".

The numerous illustrations are good and the references adequate. R. S. HARTLEY

Annual Reports on the Progress of Chemistry for 1949

Volume XLVI. 1950. Pp. 333. London: The Chemical Society. Price, 25s. 0d.

This ever welcome review begins as usual with GENERAL AND PHYSICAL CHEMISTRY, which is divided into twelve sections. The report itself marks a transition stage, and, instead of the comprehensive stocktaking of work over a period of years in selected topics, it is proposed for the future to aim at a general perspective of the main developments during the year reviewed. The papers now cited have been selected so as to give preference to those likely to interest chemists outside the immediate circle of specialists, but topics under active controversy have been included. The sections are— (1) *General Thermodynamics and the Evaluation of Thermodynamical Functions for Gases.* (2) *Isotope Chemistry.* (3) *Bond Structure and Bond Properties.* Here an illustration of particular interest to chemists arises in the microwave spectra of methylcyanide and *iso*cyanide, in which the hyperfine structure of the rotational-energy levels shows that the nuclear interaction effects are considerably larger in the cyanide. Much progress also continues to be made in purely mathematical calculations of bond structures, particularly of aromatic molecules, and this branch of mathematical chemistry is rapidly attaining major importance. Based on such calculations, it is claimed that several non-benzenoid aromatic hydrocarbons so far unknown should be reasonably stable once they were formed, and an empirical equation, with theoretical calculations, has been proposed for the resonance energy of polycyclic aromatic hydrocarbons. Experimental techniques for investigating the mechanism of organic reactions have become progressively more rigorous from the physicochemical standpoint, and increasing attention has been paid to quantitative data on the various bond parameters involved. (4) *The Structure and Properties of Liquids.* Ultrasonic measurements continue to be fairly numerous, since they give interesting information about molecular motions in liquids composed of macromolecules. (5) *The Physical Chemistry of Liquid and Solid Dielectrics*, and (6) *The Physical Chemistry of the Solid State.* A great volume of work continues to be published on (7) *Adsorption and Surface Chemistry* and (8) *Electrochemistry and Ionic Chemistry.* With respect to (9) *Kinetic Studies, Photo-reactions and Autoxidation*, reference should be made to three recent symposia on hydrocarbon oxidation and to various papers on the oxidation of hydrocarbons and related molecules in the gas

phase. (10) *The Physical Chemistry of Macromolecules* contains references to statistical studies on rubber-like molecules, and to new experimental tests and theoretical discussions on the structure and thermodynamics of rubber, polythene, and rubber–liquid systems. Under (11) *Magnetochemistry*, the possible relationship between catalytic activity and paramagnetism is discussed, and under (12) *Metals and Alloys—the Pauling Hypothesis*, an attempt is made to clarify the various hypotheses extant relating to the metallic bond.

In the second chapter, on CRYSTALLOGRAPHY, an attempt is made to combine a short account of technical developments in X-ray analysis with a survey of structure analyses in the inorganic field alone during the years 1947–1949, leaving a survey of the organic field as a whole to next year.

The third chapter, on INORGANIC CHEMISTRY, gives a balanced picture, based on the periodic groups, of the sustained and increasing attention now paid to this field of activity.

The fourth and largest chapter, on ORGANIC CHEMISTRY, represents a first step towards implementing the new general policy outlined at the start. Since this involves a formidable leeway to be made good, the present review deals mainly with some of the more important topics which have been only partly covered in the past, viz. *Long-chain Aliphatic Compounds, Vitamin A and Related Polyenes, Amino-acids, Alkaloids, Proteins*, and certain aspects of *Theoretical Organic Chemistry* such as heterolytic substitution. Only in the section on *General Methods* has a true Annual Report been presented. Under *Electrophilic Substitution*, the subject of aromatic nitration receives comprehensive treatment, the proof that the nitronium ion NO_2^+ is the nitrating agent under the usual conditions employed in aromatic nitration being given in detail. Aromatic sulphonation, which in many respects resembles aromatic nitration, and aromatic halogenation, which is even more subject to the incidence of catalytic effects than is nitration or sulphonation, also receive considerable attention. The section on *General Methods* includes reduction and hydrogenation (where the usual method of preparation of Raney nickel has been modified to produce more active catalysts, and where some correlations between activity and the preparative process have been made), addition reactions (keten and diketen), condensations (aldol type, Mannich reaction, Claisen condensations), formation of halides from silver salts of carboxylic acids, esterification, and urea complexes with linear aliphatic compounds.

BIOCHEMISTRY, the fifth chapter of the Report, contains a selection of topics from fields in which notable advances have been recorded during the year, viz. *Hæmopoietic Factors* and *Carotenoids, Vitamin A, and Visual Pigments*.

The sixth and final chapter is devoted to ANALYTICAL CHEMISTRY, and it is noted that 3500 papers are summarised in Section C of British Abstracts for 1949. This chapter follows the pattern of its predecessors in presenting accounts of certain discrete topics, viz. organic and gravimetric analysis, and the analytical applications of Raman spectra and of organic reagents, in order to bring up to date the reviews of some topics and to repair other omissions. The report on gas analysis shows the extent to which physical methods have supplemented or supplanted classical methods in the past decade, and the section on radioactivation analysis describes a new and powerful technique of great sensitivity.

This 1949 Report should be in the possession of every chemist. H. H. HODGSON

A Manual of Organic Chemistry for Advanced Students

Volume 1

The Compounds of Carbon, Hydrogen, Oxygen, and the Halogens

By G. M. Dyson. 1950. Pp. xiii + 984 with 2 folding tables. London: Longmans, Green & Co. Price, 63s. 0d.

This monumental volume is the first of a set of three which have been designed in sufficient detail to enable the practitioner in organic chemistry to gain a working knowledge of any subdivision in which he or she may be interested. The scope of the manual has naturally no reference to syllabuses or examinations, but it does attempt to provide a guide to the student during the final years of graduation and afterwards for the first few years of postgraduate research or teaching. The complete work may then prove to be a standard handbook on organic chemistry in the immediate future, and so fill a glaring gap in British chemical literature.

The eleven chapters of the book (every one of which other than the first contains an appendix giving literature references) comprise—(*I*) *Introduction*, which gives a full and most serviceable picture of the specialised literature of organic chemistry including journals other than British dictionaries, and patent literature (so necessary, because data may appear therein without reference elsewhere); (*II*) *Nomenclature*, a chapter which will prove of real use to all workers in the subject; (*III*) *Hydrocarbons* with appendixes on reference works, the petroleum industry, rubber and its analogues, and the Friedel–Crafts reaction; (*IV*) *Halogen Compounds of Hydrocarbons*; (*V*) *Alcohols, Phenols and Ethers*, including epoxides, furans, and cyclic ethers, and with appendixes on pyrenes and plant pigments, photographic developers, and fermentation and enzyme action; (*VI*) *Aldehydes and Ketones*, with appendixes on ring ketones and their relation to musk odour, plastics (including cellulose plastics, Perspex, vinyl types, hydrocarbon plastics, nylon, phenol–formaldehyde, glyptals, and silicones), and organic photosynthesis; (*VII*) *Ketens and Polyketides*; (*VIII*) *Acids and Esters*, with appendixes on the tannins, the active methylene group (malonic ester derivatives, cyanoacetic ester, diketone syntheses), and fats, waxes, and soaps; (*IX*) *Terpenes and Related Compounds*, with a discussion of the biogenesis of the terpenes and the organoleptic properties of organic substances (true sapidity, pungency, pungent compounds, odour, and the perfumery industry); (*X*) *Polyalcohols, Carbohydrates and*

Related Compounds, in which comprehensive sections appear on starches, cellulose, hemicelluloses, polyuronic acids, lignin, and pectins, chitin, and related substances, with appendixes on glycosides (including those of the plant pigment series) and sweetening compounds; (*XI*) *Steroids and other Substances of Biochemical Interest*, including vitamins, hormones, bile acids, etc.

Each of the above chapters covers general subject matter, while the appendixes deal more fully with important subjects, either by a detailed account of some piece of research, or of some practical application. Space is also given for brief summaries of borderline topics, and two separate folding tables show the "Synthetic Products from the Cracking of Petroleum", and the synthesis of "Elastic Materials", respectively.

The choice of references to original literature avoids undue multiplication by referring either to the first discovery of a substance, or the earliest discussion of a topic, or to summaries or individual papers of importance, while the comprehensive index occupies 48 pages of the book.

The author is to be congratulated on attempting a task of this magnitude and thereby providing British students, both young and old, with a serviceable guide through the complexities of modern organic chemistry. A word of appreciation is also due to the publishers for the excellence of the general presentation. H. H. HODGSON

Reports on German Industry

Joseph Voegele A.-G., Mannheim
Roller Mills for the Paint, Lacquer, and Printing Ink Industries

FD 616/50* (PB 43,533–43,537; part of PB 13,094; Microfilm C 51).

Microfilm copies of illustrated catalogues and drawings. C. O. C.

Henkel & Cie., Düsseldorf
Textile Assistants, Soaps, Wetting Agents, etc.

FDX 821* (PB 74,580; Microfilm 284 J).

A series of reports, written in 1938–44, on the use of fatty acids from the oxidation of paraffin hydrocarbons in the production of textile assistants, soaps, wetting agents, etc. C. O. C.

I.G. Farbenindustrie A.-G., Krefeld-Uerdingen
Organic Chemicals, Dyes, Intermediates, Solvents, and Resins

FDX 823* (PB 74,054; Microfilm 231 BB).

Numerous manufacturing and laboratory methods of preparation, written mostly in 1946 but a few in 1931–45. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Plastics—Dyes

FDX 836* (PB 82,043; Microfilm X 31).

Reports, written mostly in 1942–44, on various aspects of the manufacture and application of various plastics. Others give details for the works production of the following dyes—

Auracin G
Auramine
Chrysolin A
Diamond Phosphine D and R
Eosine G conc. for ink and I crystals
Erythrosin AGZ
Euchrysin 2GNX
Fast Acid Pink B, Violet ARR
Irisamine S
Pyronin G
Rhodamine B and 6G
Rhodulin Orange NO
Victoria Blue conc.
Violamine Ia3G

all of which are used in three-colour photography. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Plastics, Dyes, Intermediates, Textile Finishing and Auxiliary Agents, Synthetic Rubber

FDX 820* (PB 74,622; Microfilm L 86).

A large number of reports, written in 1937–40, dealing mostly with the production of dyes and intermediates, others dealing with various aspects of the production, properties, and uses of textile finishing agents and assistants, and of synthetic resins and rubbers. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Polyurethans—Dyeing Assistants
Phthalocyanine and Polymethin Dyes and Intermediates for them
Intermediates for Dyes for Resins
Wetting Agents and Detergents

FDX 811* (PB 73,900; Microfilm N 68).

Among a large number of reports dealing mainly with synthetic rubber and plastics are some, written in 1937–44, dealing with the manufacture and spinning of polyurethans, phthalocyanine and polymethin dyes and their intermediates, intermediates for dyes for resins, cellulose, and polyvinyl compounds, levelling agents in dyebaths, dyeing and textile assistants, etc. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Textile Chemicals and Assistants—Solidogens
Animalisation of Cellulosic Fibres
Dyes—*iso*Cyanates and Polyurethans

FDX 819* (PB 73,916; Microfilm N 67).

A series of reports dealing mainly with plastics, but including some written during 1936–44 on—textile chemicals and assistants; Solidogens; animalisation of cotton and viscose and cuprammonium rayons, and improving the fastness of dyeings on the animalised fibres; developers for basic dyes; gallocyanine, phthalocyanine, acetate rayon, and other dyes; *iso*cyanates and polyurethans and fibres from them. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Intermediates and Dyes—Textile Chemicals
Synthetic Tanning Agents—Chlorinated Rubber

FDX 833* (PB 74,946; Microfilm T 32).

A large number of reports, written in 1936–44, over half of them dealing with azo and azoic dyes and their intermediates. Others deal with Tanigan Extra A and B, light-absorptive protective agents, and a few with textile chemicals and chlorinated rubbers. C. O. C.

I.G. Farbenindustrie A.-G., Frankfurt a. M.
Lead Cyanamide, Mowilith, Desmodur and Desmophen, Resin AW2, Atephen

FD 615/50* (PB 43,532, 43,538–43,541, part of PB 13,094; Reel C 51).

Microfilm copies of five reports, written in 1943–45, one of which describes trials with lead cyanamide and red lead, it being shown that lead cyanamide is the better both from the point of view of rust protection and ease of incorporation into paint. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Dressing, Dyeing, and Mothproofing of Furs
Pigments for Carpets, Rubber, and Plastics
Printing Inks

FDX 826* (PB 74,737; Microfilm 108 M).

Six reports, written in 1939–44, on fur dressing, dyeing, and mothproofing, one describing the mothproofing of silver fox furs with Eulan NKF extra. They are followed by

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

38 reports, written in 1935–44, on various aspects of the preparation of pigments, paints, and printing inks. One report deals with the application of sheets or emulsions of plastics to render the latter washable, and another deals with the use of pigment–resin emulsions for colouring carpets. C. O. C.

Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

I—PLANT; MACHINERY; BUILDINGS

Carbon Black Plant [of Cabot Carbon Ltd., Ellesmere Port, Cheshire]. *International Chem. Eng.*, **31**, 351–354 (Aug. 1950).

An account of the plant and the process used, illustrated by photographs and a flow sheet. C. O. C.

Layout of a Modern Dyehouse. C. E. Müller. *Textil-Praxis*, **5**, 504–506 (Aug. 1950).

Particular stress is laid on the advantages of enclosed vats, winches, and jigs, especially with regard to economy in steam and improved working conditions. Water and heating systems and internal transport are amongst the other points discussed. B. K.

PATENTS

Pelleting Carbon Black. T. H. Whaley and Texas Co. *U.S.P.* 2,511,088.

Continuous Pelleting of Carbon Black. G. P. Bunn and Phillips Petroleum Co. *U.S.P.* 2,511,901.

Continuous Wool Scouring. G. C. Weinpel and Botany Worsted Mills. *U.S.P.* 2,509,464.

Apparatus is described which results in wool of better quality and greater recovery of wool grease combined with lower overall alkalinity treatment. C. O. C.

Treating a Tow of Filaments or Threads in a Limited Space. J. F. Keggin and I.C.I. Ltd. *B.P.* 642,359.

A continuous tow of filaments is treated in absence of tension with a liquid of sp. gr. > that of the tow. The tow is carried by the liquid through a tube whose end portion progressively increases in width and leads to another tube which is wider than the narrowest portion of the first tube. The upper surface of this second tube is at a lower level than the overflow level of the liquid. The speed of the liquid through the tubes and the inclination upwards in the direction of flow of the liquid of the upper surface of the second tube are such that the tow collects against this upper surface and is retained there long enough for the liquid to produce the effect desired. C. O. C.

Liquid-extracting Press for Drying Fibrous Materials. J. Stadler. *U.S.P.* 2,510,764.

The material is compressed in a high-pressure power press of the cylinder and piston type. C. O. C.

Seal for Strand-coating Apparatus. J. E. Lodge and Western Electric Co. Inc. *U.S.P.* 2,507,310.

Thread Coating. D. K. Alpern, H. M. Freydberg, W. H. Hawkins, and Freydberg Bros.–Strauss Inc. *U.S.P.* 2,509,407.

Register Control Systems for Moving Webs. J. F. Crosfield Ltd. and J. F. Crosfield. *B.P.* 641,830.

Pedal Mechanism for Lifting the Cutters of Cloth-shearing Machines. Zbrojovka Brno N.P. *B.P.* 641,263.

Washing, Dry Cleaning, or Garment Dyeing Machines. Isaac Braithwaite & Son Engineers Ltd. and T. B. Walker. *B.P.* 640,974.

Laundry Drying and Fluffing Machine. M. Troy. *U.S.P.* 2,506,476.

Laundry Calenders. Manlove, Alliott & Co. Ltd. and W. A. Hastie. *B.P.* 641,014.

Presses for Ironing the Sleeves of Garments. Prosperity Co. Inc. *B.P.* 641,833.

Glove Ironing Machine. T. G. Boldizzoni. *U.S.P.* 2,511,455.

Turning and Pressing Gloves. T. G. Boldizzoni. *U.S.P.* 2,511,456.

Stretching and Drying Device for Fabric. S. J. Brewczynski and J. Brewczynski. *U.S.P.* 2,508,353.

A stretching and drying device for sheets of cloth of irregular perimeter, e.g. doilies, is described. C. O. C.

Coating Paper. C. R. Outterson, B. A. Ford, and Albemarle Paper Manufacturing Co. *U.S.P.* 2,508,287.

Applying Transfers to Ceramic Blanks. British United Shoe Machinery Co. Ltd., C. H. James, and J. W. Pratt. *B.P.* 642,162.

Dry Scouring of Greasy Wool or Wool Wastes. P. Townsend. (VII, p. 602.)

II—WATER AND EFFLUENTS

Purification of Textile Effluents. W. Merkel. *Textil-Praxis*, **5**, 530–534 (Aug. 1950).

Effluents from textile factories may be contaminated with mechanical impurities or chemical impurities of various kinds. The latter may attack concrete or iron in buildings, destroy fish life, or decompose to liberate unpleasant or even poisonous gases. Methods of purification are described, employing chemical, mechanical, or biological processes or a combination of these. B. K.

The Niers [Pista] Process for Purifying Textile Effluents. H. Jung and W. Schröder. *Textil-Praxis*, **5**, 534–538 (Aug. 1950).

Textile and dyehouse effluents can be purified by treatment with iron filings and oxygen. The iron is converted into ferric hydroxide in an active state, which has strong flocculating properties. The Pista process is a slight modification of the German process and operates in Switzerland. B. K.

Synthetic Detergents and Sewage Processing. I—Introduction. M. Elton. *Inst. Sewage Purification J. & Proc.*, 351–354 (1949). **II—Sedimentation of Sewage, etc.** A. Sciver. *ibid.*, 354–359. **III—Production of Methane from Sewage Sludge.** P. N. Degens, H. van der Zee, J. D. Kommer, and A. H. Kamphuis. *ibid.*, 359–365. **IV—Processing of Sewage containing Wool Scouring Liquors, etc.** H. C. Evans and P. A. Winsor. *ibid.*, 365–370: *Chem. Abs.*, **44**, 6061 (10th July 1950).

I and II—Maximum effect of 20 p.p.m. Teepol was to increase turbidity and oxygen consumption of settled sewage by 2·8% in each case. Increase of Teepol content increased the adverse effect.

III—As the cleaning efficiency of synthetic detergents is greater than that of fatty acid soaps, substitution of the former for the latter decreases CH_4 production.

IV—Centrifugal separation of grease from wool scouring liquor is not impeded by substitution of Teepol for soap, nor is cracking affected if the liquor is cooled before acidifying or if 0·8–1·6% alumino-ferric is added before acidifying to pH 3·5 at either 50 or 20–30°C., well clarified effluents containing approx. 33% of the Teepol used being obtained by the latter procedure. When sewage is tested by the method of Jones (*Chem. Abs.*, **39**, 3951 (1945)) it often shows an apparent content of synthetic detergents even in absence of the latter, which is probably due to presence of compounds containing a hydrocarbon group in combination with an SO_4Na or SO_3Na group. Such compounds are derived from urine. Alkaline wool-scouring liquors also show an apparent synthetic detergent content in absence of such reagents, probably derived from degradation of the wool. In the laboratory addition of Teepol to give 40 p.p.m. Na *sec.*-alkyl sulphate had no apparent effect on settling of unacidified sewage. Addition of 10 p.p.m. had some effect, which varied with different samples, in the case of acid precipitation, but sewage containing up to 40 p.p.m. can be precipitated satisfactorily by adding 80 p.p.m. alumino-ferric before acidifying to pH 3·5. The increase in volume of the sludge is not incommensurate with the increased purification obtained. C. O. C.

Characteristics and Treatment of Wool-dyeing Effluents. J. A. McCarthy. *Sewage & Industrial Wastes.* **22**, 77–86 (1950): *Chem. Abs.*, **44**, 6064 (10th July 1950).

Wool-dyeing wastes are stronger than domestic sewage but weaker than wool-scouring wastes. Sedimentation and coagulation are not effective. The wastes can be treated on trickling filters with loadings of 1000–5000 lb./acre-ft. Recirculation is beneficial. High or low pH reduces efficiencies. C. O. C.

Treatment of Cotton Printing and Finishing Wastes. S. E. Coburn. *Ind. Eng. Chem.*, **42**, 621–625 (April 1950).

A pilot plant was operated to determine the relative merits of a high-rate trickling filter and a chemical treatment plant to meet the fairly stringent requirements of the Delaware River Basin authorities. It was concluded that the chemical treatment plant would be cheaper to build (by about 10%) but its running costs would be over double (about 12% per year of the capital). The difference in running costs is mostly due to the cost of chemicals and labour. In addition the disposal of sludge is a greater difficulty with the chemical plant. The pilot plant used is described, and the estimates were based on a handling capacity of 2,000,000 gal. per day. W. J. M.

Treatment of Cotton-finishing Waste Liquors. G. G. Bogren. *Ind. Eng. Chem.*, **42**, 619–621 (April 1950).

Pilot-plant experiments for a high-rate trickling filter are described for treating the effluent from caustic and peroxide kiers, bleaching, dyeing, mercerising, and sundry other processes. At present heavy effluent only is treated. The object of the experiments is to provide a basis for designing a suitable plant for full treatment of all the effluent. It is concluded that B.O.D. (biological oxygen demand) removal of at least 60% is possible at a filtration rate of 10,000,000 gal. per acre per day in a properly designed plant. W. J. M.

PATENT

Recovery of Metal Ions from Solutions. A.S.P. Chemical Co. Ltd., C. L. Walsh, and B. A. Adams. *B.P.* 641,918.

The solution containing the metal ions is passed through a bed of an insoluble pectic substance having exchangeable cations, e.g. H^+ or Ca^{++}. This converts all the pectic substance into the metal salt, the metal then being removed by treating the exhausted bed with a solution of an acid or a salt. C. O. C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Annual Review of Literature on Fats, Oils, and Soaps— II. M. M. Piskur. *J. Amer. Oil Chem. Soc.*, **27**, 211–233 (June 1950).

Future of Synthetic Detergents in relation to the Petroleum-chemical Industry. A. K. Simcox. *Chem. and Ind.*, 178–182 (11th March 1950).

The development of synthetic detergents is described. There has been a transition from fatty raw materials to mineral oils, brought about to a great extent by the war and the world food situation, but the modern synthetic detergents now stand in their own right and are increasing in popularity. Soaps form a fairly large proportion of the products from edible oils, but the equivalent synthetic detergent production is a small fraction of the world mineral oil resources. The importance of this is evident at the present day, when the population of the world is rising rapidly and there is an ever increasing demand for foodstuffs. W. J. M.

Variations in Surface Activity of Aqueous Solutions of Sodium Alkyl Sulphates in presence of Polar–Non-polar Molecules. L. Desalbres. *Bull. Soc. chim. France*, 26–28 (1950): *Chem. Abs.*, **44**, 6705 (10th Aug. 1950).

Presence of *cyclo*hexanol, 8-hydroxy-*p*-menthane, or terpineol causes very sharp decrease in the surface tensions of aqueous solutions of sodium dodecyl sulphate at 25°C. with increase in concentration of the sodium dodecyl sulphate. Presence of 8-hydroxy-*p*-menthane and terpineol causes a marked minimum in the surface tension–concentration curve, which is not shown in presence of *cyclo*hexanol or of sodium dodecyl sulphate alone. C. O. C.

Preparation and Properties of some *NN'*-Dialkylethylenediaminediacetic Acids. A. E. Frost and A. E. Martell. *J. Amer. Chem. Soc.*, **72**, 3743–3746 (Aug. 1950).

NN'-Dialkylethylenediaminediacetic acids have been prepared from dibutyl-, dioctyl-, didodecyl-, di*cyclo*hexyl-, and dibenzyl-ethylenediamine. Titration and absorption spectra studies indicated that all the amino acids except the di*cyclo*hexyl derivative formed strong chelates with copper ions, while titration data indicated only weak chelation with calcium ions. C. O. C.

Mildew-resistant Size for Tent Twill Warps. J. H. Brant.

ORR 188/50* (PB 67,504).

Carboxymethocel A (an Al salt of cellulose glycollic acid), Stymer (a styrene derivative), Rhoplex NR (an acrylic resin), and Aerotex 625 (a resin of unknown type) are as good as or better than starch for sizing warps for tent twills and other cloths where the size is left in the finished product, and have the advantage of being resistant to mildew. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C.— see J.S.D.C., **66**, 53 (Jan. 1950).

Amylose Complexes. W. J. Katzbeck and R. W. Kerr. *J. Amer. Chem. Soc.*, **72**, 3208–3211 (July 1950).

Amorphous amylose has been prepared. When solid it adsorbs only traces of butyl alcohol vapour, fatty acid, and about 4% of iodine; the latter being less than that adsorbed by amylose in the frozen gel and retrograded states. These facts are proof that amylose complex formation is not an adsorption phenomenon. Only the "V" form of amylose takes up significant quantities of iodine vapour, butyl alcohol, and fatty acid, confirming that a particular molecular configuration is necessary for complex formation; the latter is assisted by presence of moisture, and so its effect seems to be physical rather than chemical. C. O. C.

PATENTS

Wetting Agents or Detergents. Standard Oil Development Co. *B.P.* 641,439.

High-grade products are obtained by extracting a petroleum hydrocarbon fraction with a preferential solvent for its aromatic constituents, separating the extract from raffinate and solvent, and alkylating it with the polymer of one or more C_3–C_4 olefins of b.p. 150–350°F., and finally sulphonating the alkylate. C. O. C.

Surface-active Agent useful as a Detergent, Finishing Agent, Softener, and Wetting Agent. Sun Chemical Corpn. and W. Kaplan. *B.P.* 640,924.

A sulphonated high-mol.wt. unsat. aliphatic nitrile of > 9 C is used. C. O. C.

Surface-active Organic Sulphonates. E. E. Gilbert, J. A. Otto, and Allied Chemical & Dye Corpn. *U.S.P.* 2,506,417.

Products useful as detergents, wetting and dispersing agents, softening agents, etc. are prepared by condensing acetaldehydedisulphonic acid at ordinary temperature with an alkylbenzene containing at least one aromatic H atom. C. O. C.

Propylene Glycol Monoaryl Ether–Esters of Sulphosuccinic Acid (Sodium Bis(2-aryloxy*iso*propyl) Sulphosuccinates). E. C. Britton, R. L. Brown, and Dow Chemical Co. *U.S.P.* 2,510,008.

The alkali-metal salts of sulphosuccinic acid diesters of propylene glycol phenyl ether, propylene glycol 4-chlorophenyl ether, propylene glycol 2:4-dichlorophenyl ether, or propylene glycol 2:4:6-trichlorophenyl ether, e.g.—

$$\begin{array}{l} CH_2{\cdot}CO{\cdot}O{\cdot}CH(CH_3){\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}Cl \\ | \\ NaSO_3{\cdot}CH{\cdot}CO{\cdot}O{\cdot}CH(CH_3){\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}Cl \end{array}$$

are detergents and emulsifying agents of extraordinary wetting power. They are soluble in water and many organic solvents. Aqueous emulsions formed with their aid are unusually stable to acids and alkalis. C. O. C.

Detergent Composition. Deodor-X Co. of England Ltd., P. J. Hooper, and R. A. Chandler. *B.P.* 641,902.

A mixture of 77% by weight of a detergent or wetting agent, 19·5% of formaldehyde, and 3·5% of sodium

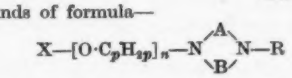
metasilicate is used for cleansing, disinfecting, and deodorising fabrics contaminated with evil-smelling soils. C. O. C.

Germicidal Detergents. General Aniline & Film Corpn. and J. M. Lambert. *B.P.* 641,297.

An organic anionic detergent, e.g. a sodium soap of a higher fatty acid, is mixed with an organic cationic germicide, e.g. cetylpyridinium chloride, in relative proportions by wt. of 1 : 4 to 12 : 1, with addition of a non-ionic surface-active agent containing a polyglycol ether group, e.g. a water-soluble polyethylene oxide derivative of di*iso*butylphenol, to the extent of at least 10% by wt. on the previous two combined. J. W. B.

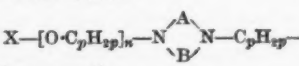
NN′-Disubstituted Piperazine Derivatives. J. Ross, J. D. Malkemus, and Colgate-Palmolive-Peet Co. *U.S.P.* 2,508,652.

Compounds of formula—



(X = a long-chain aliphatic radical of 6–24 C which may contain a CO group to link it to the rest of the molecule; A and B = unsubst. ethylene radicals or ethylene radicals having 1–4 C_{1-3} Alk substituents; R = an alkyl or acyl radical of 1–3 C; n = 1–9; and p = 2–4) have excellent foaming, detergent, wetting, and limesoap-dispersing properties. *U.S.P.* 2,508,653.

Compounds of formula—



have similar properties. C. O. C.

Surface-active Organic Nitrosation–Sulphitation Products in Multivalent Metal Salt Form. W. A. Fessler and Allied Chemical & Dye Corpn. *U.S.P.* 2,510,466.

The products obtained by treating water-soluble salts of nitrosation–sulphitation products (e.g. those obtained by the processes of *U.S.P.* 2,265,993, 2,336,387, and 2,313,719) with water-soluble salts of multivalent metals in water and an alcoholic solvent of low water-solubility, e.g. amyl alcohol, have good solubility in many organic water-immiscible solvents as compared with the corresponding alkali-metal and ammonium salts and have valuable surface-active properties. Thus the Al salt is soluble in trichloroethylene, wherein it exerts dry cleaning action, the Cu salt is a rotproofing agent for fibres, and the Mg salt is an effective emulsifying agent. C. O. C.

Modified Starch. National Starch Products Inc. *B.P.* 641,222.

Modified starch, possessing inhibited gelatinisation when dispersed in water under normal gelatinising conditions, is prepared by treating ungelatinised starch with a bifunctional ether-forming reagent, e.g. epichlorohydrin, which forms ether linkages with two hydroxyl groups of the starch molecules. J. W. B.

Size for Saponified Stretched Cellulose Acetate Rayon. British Celanese Ltd. *B.P.* 640,989.

A composition made from casein or soya-bean protein, an alkylolamine, and oleic acid gives excellent weaving properties, which are retained even on aging. C. O. C.

Antistatic Agents. H. F. Oxley, E. B. Thomas, and British Celanese Ltd. *B.P.* 641,580.

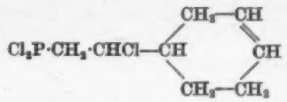
The diethylamine salts of organic sulphonic acids, particularly of aliphatic sulphonic acids, are excellent antistatic agents, and have the advantage that they are readily miscible with the usual lubricating oils used on the fibres. C. O. C.

Polyvinyl Acetate Emulsions containing Glyoxal. W. D. Robinson and Du Pont. *U.S.P.* 2,510,257.

Aqueous emulsions of polyvinyl acetate, containing not < 30% by weight of water, enough water-soluble polyvinyl alcohol to act as an emulsifying agent, and 0·1–1·0% on the total weight of solids, yield water-insensitive films, etc. after drying. C. O. C.

2-Chloro-2-(3′-*cyclo*hexenyl)ethyldichlorophosphine. E. C. Ladd, J. R. Little, and United States Rubber Co. *U.S.P.* 2,510,699.

The compound—



is a chemically modifying agent for treating polymeric materials, particularly those containing hydroxyl groups, e.g. cellulose or polyvinyl alcohol. C. O. C.

Increasing the Fastness of Coloured Cellulose Esters or Ethers to Gas Fading. H. C. Olpin and W. B. Miller. *B.P.* 641,459.

The acyclic amidines of carboxylic acids containing an aromatic radical, e.g. *N*-phenylbenzamidine, are very useful agents for imparting resistance to gas fading. They are substantive to cellulose acetate and fast to washing, and impart some protection against loss in strength of cellulose acetate by the action of ultra-violet radiation. C. O. C.

Softening and Water-repellent Agents. E. Zerner, P. I. Pollak, and Sun Chemical Corpn. *U.S.P.* 2,510,007.

A fatty acid amide of 12–30 C, or a mixture of a fatty acid of 12–30 C with a nitrile or amide of a fatty acid containing the same number of carbon atoms, is heated at 300–350°C. until the acid number is < 16·1. The product is then chloromethylated, and finally treated with a tertiary amine. The final product imparts a water-repellent finish to textiles which is highly resistant to dry cleaning and laundering. C. O. C.

Water-repellent Agents. J. B. Rust, Montclair Research Corpn., and Ellis-Foster Co. *U.S.P.* 2,510,522.

A water-dispersible composition, which imparts to textiles a water-repellent finish fast to dry cleaning, is obtained by heating (*a*) a tertiary amine, (*b*) HCl, HBr, PCl_3, $POCl_3$, PCl_5, SO_2Cl_2, or $SOCl_2$, and (*c*) a preformed condensate of (i) an aliphatic amide of < 10 C and (ii) an *N*-alkoxymethyl derivative of urea or melamine containing not > 5 C in each alkoxy group, of which it contains > 1. C. O. C.

Unpolymerised Urea–Formaldehyde Reaction Products. Du Pont. *B.P.* 641,703.

Highly stable solutions of hydroxymethylureas are obtained by mixing 50–70 parts of formaldehyde with 100 of water at > 45°C., keeping the resulting formalin at > 45°C., and then mixing with urea at pH 7–9, using 1 mol. urea to 3·9–10·0 mol. formaldehyde, the resultant liquid being kept at least momentarily at 70–90°C. The solutions can be kept for long periods. C. O. C.

Water-soluble Urea–Formaldehyde Resin. Beck, Koller & Co. (England) Ltd. and P. S. Hewett. *B.P.* 641,697.

A clear, stable, water-soluble resin is obtained by heating 1 mol. urea and 2–2·5 mol. formaldehyde (as 37% formalin) in presence of a borax–boric acid buffer to maintain pH 6·7–7·3 so as to form only hydroxymethylurea, and then adding 1–2·5% by weight of the total materials of boric acid and continuing heating to condense the hydroxymethyl groups through the methylene and/or ether linkage. The resin is selectively absorbed by cellulosic materials from aqueous solution. It imparts abrasion resistance and dimensional stability to textiles, adheres well to glass fibres, and imparts wet strength to paper. C. O. C.

Arylsulphonamide-modified Melamine Resins. M. J. Scott and Monsanto Chemical Co. *U.S.P.* 2,508,875.

Heating 1 mol. of a methylolmelamine–alcohol condensate with 0·1–1·0 mol. of benzenesulphonamide or a nuclearly alkylated benzenesulphonamide yields transparent resins useful for finishing textiles, in surface coatings, etc. C. O. C.

Aqueous Emulsions of Alkyl Silicon Esters or Polymers. W. E. Langrish-Smith, C. Shaw, H. G. Emblem, and Silicon (Organic) Developments Ltd. *B.P.* 641,553.

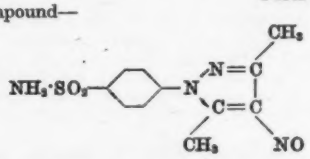
Silicon esters may be emulsified by agitating them in water with < 5% of their weight of an organic base having pK_a value > 7·5 but not > that of piperidine, e.g. piperidine, morpholine, or *cyclo*hexylamine, and an emulsifying agent. The resultant emulsions may be used for fireproofing textiles, for delustring rayon, or as anti-slip agents. C. O. C.

Tetrachlorothiophen Dichloride— Insecticide and Fungicide. Pennsylvania Salt Manufacturing Co. *B.P.* 641,094.

Tetrachlorothiophen dichloride, obtained by chlorinating, in absence of a catalyst, thiophen or a thiophen derivative containing < 6 C, has excellent insecticidal and fungicidal properties. C. O. C.

1-*p*-Sulphamylphenyl-3:5-dimethyl-4-nitroso-pyrazole — Mildewproofing Agent. N. K. Sundholm and United States Rubber Co. *U.S.P.* 2,510,726.

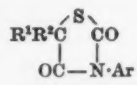
The compound—



prevents fungal growth on textiles and other organic materials. C. O. C.

3-Phenyl-2:4-thiazolediones — Rotproofing Agents. N. K. Sundholm, J. B. Skaptason, and United States Rubber Co. *U.S.P.* 2,510,725.

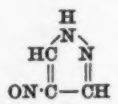
Compounds of formula—



(R^1 and R^2 = H or Alk) are effective rotproofers for textiles, etc. C. O. C.

3:5-Dimethyl-4-nitrosopyrazole—Rotproofing Agent. N. K. Sundholm and United States Rubber Co. *U.S.P.* 2,510,724.

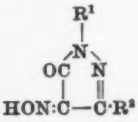
4-Nitrosopyrazoles, of parent structure—



are effective fungicides and bactericides suitable for rotproofing textiles. C. O. C.

4:5-Pyrazoledione 4-Oximes — Mildewproofing Agents. B. A. Hunter, N. K. Sundholm, and United States Rubber Co. *U.S.P.* 2,510,696.

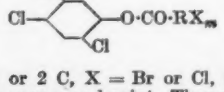
Compounds of formula—



(R^1 and R^2 = H, aliphatic, or aromatic radicals), e.g. 4:5-pyrazoledione 4-oxime, are good mildewproofing agents for textiles, etc. C. O. C.

2:4:5-Trichlorophenyl Esters of Halogenoaliphatic Acids. C. L. Moyle and Dow Chemical Co. *U.S.P.* 2,508,334.

Compounds of formula—



(R = Alk of 1 or 2 C, X = Br or Cl, m = 1 or 2) are preservatives for paper and paint. They are stable to light and air, little affected by CO_2, and non-irritating to the skin. C. O. C.

Abrasion-resistant Coatings. Du Pont. *B.P.* 640,177.

The abrasion resistance of conventional surface coatings, e.g. those based on cellulose nitrate or alkyd resins, is considerably improved by dispersing in the coating composition < 12% of polyethylene of highly crystalline structure. E. C.

Surface Coverings. United Wallpaper Inc. *B.P.* 641,938.

Wallpaper or fabric, which has a surface resistance to grease, inks, food stains, etc., and which can be readily cleansed with soap and water, is obtained by applying successively (1) an oleo-resinous ground coating, (2) a decorative coating of oleo-proteinacious water ink, and (3) an outer resinous coating. C. O. C.

Oil-soluble Metal Salt Compositions. Nuodex Products Co. Inc. *B.P.* 641,168.

Addition of not > 10% by weight on the total composition of an alkyl acid phosphate to a solution of an oil-soluble metal salt greatly reduces the viscosity of the solution and greatly improves its stability. C. O. C.

Synthetic Detergents and Sewage Processing. I— Introduction. M. Elton. (II, p. 593.)

Cellulose Nitrate Emulsions. H. C. Phillips and Hercules Powder Co. (V, p. 600.)

Melamine Resins. J. Hofton. (XIII, p. 607.)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Phenol by Sulphonation. R. L. Kenyon and N. Boehmer. *Ind. Eng. Chem.*, **42**, 1446–1455 (August 1950).

The history of phenol production in U.S.A. is narrated, the fundamental chemistry of the various commercial methods briefly described, and the Monsanto Co.'s phenol process dealt with in detail, including plant, sulphonation, neutralisation, evaporation, fusion, and phenol isolation and refining. Final sections give by-product (sulphur dioxide and sodium sulphite) processing, materials of construction, materials handling, and chemical control with specifications. There are 34 references. H. H. H.

Kinetics of the Reduction of Aromatic Nitro Compounds with Tin and Hydrochloric Acid. C. E. Vanderzee and W. F. Edgell. *J. Amer. Chem. Soc.*, **72**, 2916–2923 (July 1950).

Formation of a transitory intermediate reduction product indicates that reduction of nitro groups under the experimental conditions used proceeds not by a single step but by two or more successive steps. C. O. C.

Vapour Phase Condensation of Aniline to Diphenylamine. H. E. Hoelscher and D. F. Chamberlain. *Ind. Eng. Chem.*, **42**, 1558–1562 (August 1950).

Activated alumina is found to catalyse the vapour-phase condensation of aniline to diphenylamine in good yield, and with no side reactions or decomposition in detectable quantities. The conversion increases with increasing temperature at constant space velocity, first becoming appreciable at about 400°C., with an optimum at 460°C., above which decomposition of both aniline and diphenylamine occurs. In the equipment described, the maximum conversion was ~ 35% with an average of 20–25%. It is concluded, from the thermodynamics of the reaction, that industrial-sized equipment would increase the conversion considerably, since the reaction appears to be entirely dependent on rate factors. H. H. H.

Studies in Light Absorption— IX. E. A. Braude. *J.C.S.*, xiv (July 1950).

Correction to previous paper, *J.C.S.*, 379–384 (Jan. 1950): J.S.D.C., **66**, 297 (May 1950).

Nature of the Spectral Displacement accompanying the Adsorption of Aromatic Amines on Active Clays. A. I. Sidorova and A. N. Terenin. *Izvestiya Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 152–161 (March–April 1950).

The bright colorations which arise when various colourless aromatic amines are adsorbed from solution on to clays of the bentonite type are considered to result from the formation at the surface of the adsorbent of the positive semiquinone ion, which is then stabilised by adsorption. The blue coloration, formed by the adsorption of diphenylamine on to bentonite from the gas phase at low pressures, was examined spectrographically and found to have an absorption maximum close to the known maximum of the semiquinone ion. On admitting air and moisture the spectrum changed considerably, owing to the further reaction of the semiquinone to give the well

known blue oxidation product of diphenylamine. Bentonite was replaced in this experiment by microcrystalline preparations of various metal oxides and salts, but the blue coloration was obtained in two cases only—anhydrous copper sulphate and cerium dioxide. A yellow coloration was obtained with bismuth trichloride, but this, like the colours of solutions of amines in liquid sulphur dioxide, is to be attributed to changes in the molecule of the second component (acting as an electron-acceptor), rather than to changes in the amine itself.
A. E. S.

Influence of Water on the Coupling Power of Diazotised Amines and on Diazo-group Elimination in Aqueous Ethanol–Sulphuric Acid Media. H. H. Hodgson and J. Ratcliffe. *J.C.S.*, xiv (July 1950).

Correction to previous paper, *J.C.S.*, Supplementary Issue No. 1, S 233–S 234 (1949): J.S.D.C., **66**, 154 (Feb. 1950).

Chemistry of Diazo Compounds. II—Evidence for a Free Radical Chain Mechanism in the Reduction of Diazonium Salts by Hypophosphorous Acid. N. Kornblum, G. D. Cooper, and J. E. Taylor. *J. Amer. Chem. Soc.*, **72**, 3013–3021 (July 1950).

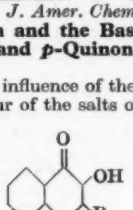
Hypophosphorous acid reduction of diazonium salts is catalysed by traces of oxidising agents and inhibited by small amounts of quinones. This, in conjunction with other facts, leads to the conclusion that reduction of diazonium salts by hypophosphorous acid is a free-radical chain reaction. A detailed mechanism is given. C. O. C.

Mechanism of Oxidation of Leuco Malachite Green by Ceric Sulphate. C. G. Swain and K. Hedberg. *J. Amer. Chem. Soc.*, **72**, 3373–3375 (Aug. 1950).

The carbinol is not an intermediate in the oxidation of leuco malachite green with ceric sulphate, because it is dehydrated to the dye more slowly than the leuco base is oxidised to the dye under comparable conditions.
C. O. C.

Hydroxynaphthaquinones. I—Colour and Acidity. M. G. Ettlinger. *J. Amer. Chem. Soc.*, **72**, 3085–3090. **II—Cyclisation and the Basicity and Interconversion of *o*- and *p*-Quinones.** *ibid.*, 3090–3095 (July 1950).

I—A study of the influence of the substituent R on the acidity and the colour of the salts of—



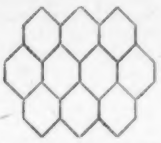
II—The interconversion of the lapachones in acid is explained from measurements of spectra and ionisation in sulphuric acid. The discussion is extended to oxidation–reduction potentials and rates and mechanisms of hydroxyquinone cyclisations. C. O. C.

Halochromism in the Anthracene Series—the Case of the Diquinol of 1-Dimethylamino*meso*-diphenylanthracene—Comparison with *o*-Dimethylaminotriphenylcarbinol. C. Dufraisse and J. Robert. *Compt. rend.*, **229**, 798–801 (1949): *Chem. Abs.*, **44**, 6272 (25th July 1950).

Absorption spectrum studies reveal a parallelism between the diphenylanthracene and triphenylmethane series. The spectra are not essentially different for the free base and the salt, indicating stabilisation due to strong hydrogen-bonding as well as steric hindrance.
C. O. C.

Benzoperylene and Benzobisanthene Derivatives. E. Clar and H. Frömmel. *Chem. Ber.*, **82**, 46–60 (1949): *Chem. Abs.*, **44**, 2967 (10th April 1950).

The synthesis of various benzoperylenes and benzobisanthenes is described. Several of these are vat dyes. Thus bisanthene is condensed with maleic anhydride in boiling nitrobenzene to give ovalenetetracarboxylic anhydride, which on heating with soda lime yields ovalene—



When oxidised with selenium dioxide in boiling nitrobenzene this gives a quinone which dyes cotton brown-yellow from a red vat. R. K. F.

4-Benzoyl*meso*benzanthrone. (The late) H. G. Rule, N. Campbell, A. G. McGregor, and A. A. Woodham. *J.C.S.*, 1816–1819 (July 1950).

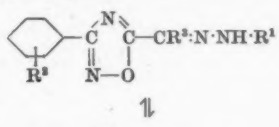
Oxidative hydrolysis of 4-*a*-cyanobenzyl*meso*benzanthrone, obtained by the condensation of *meso*benzanthrone with benzyl cyanide, affords an excellent method for the preparation of 4-benzoyl*meso*benzanthrone. The constitution was established via the sequence—1-bromo-4-methylnaphthalene → 1-bromo-4-benzoylnaphthalene → 4-benzoyl-1-naphthonitrile cyclised to 4-cyano*meso*benzanthrone, which was hydrolysed to the 4-carboxylic acid and then converted to 4-benzoyl*meso*benzanthrone. Oxidation of the latter gave 2-benzoylanthraquinone-1-carboxylic acid, previously obtained from 1-chloro-2-benzoylanthraquinone (Scholl *et al.*, *Ber.*, **69**, 2428 (1936)).
H. H. H.

Spectral Changes of Pinacyanol Chloride in Sodium Silicate–Salt Solutions. R. C. Merrill and R. W. Spencer. *J. Amer. Chem. Soc.*, **72**, 2894–2899 (July 1950).

Addition of salts to solutions of pinacyanol chloride in aq. sodium silicate reduces the effect of the latter on the absorption spectra of the dye. Experiments are described, the results of which indicate that this is due to the salts affecting the absorption spectra of the dye directly as well as by influencing aggregation. C. O. C.

Colour Development in presence of Coloured Couplers—I. R. Merckx. *Science et Inds. phot.*, **21**, 45–49 (1950). **II.** *Ibid.*, 84–86: *Chem. Abs.*, **44**, 6753 (10th Aug. 1950).

I—The coupling reactions of the azo derivatives of some 3-phenyloxadiazoles of formula—



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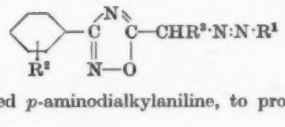
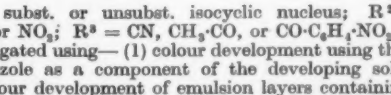


with oxidised *p*-aminodialkylaniline, to produce dyes of formula—



(R^1 = subst. or unsubst. isocyclic nucleus; R^2 = H, CH_3, or NO_2; R^3 = CN, $CH_3{\cdot}CO$, or $CO{\cdot}C_6H_4{\cdot}NO_2$) were investigated using—(1) colour development using the azo-oxadiazole as a component of the developing solution, (2) colour development of emulsion layers containing the azo derivative, and (3) coupling in solution. Detectable amounts of the azomethines were formed only when R^3 = CN.

II—With oxidised *p*-aminodiethylaniline azo derivatives of acetylacetone, acetanilide, 1-phenyl-3-methyl-5-pyrazolone, and 1:3-diketoindane do not yield azomethine dyes. Azo derivatives of *p*-methylcyanoacetophenone, cyanoacetanilide, malononitrile, benzothiazolylacetonitrile, *p*-nitrophenylacetonitrile, and 2:4-dinitrophenylacetonitrile yield azomethines by elimination of the azo group. It is probable that an essential condition for azomethine dye formation in these cases is the presence of the CH group adjacent to the C atom bearing the amino group.
C. O. C.

Fluorescence of Magnesium Phthalocyanine and of Chlorophyll under Various Conditions—Complex Structure of the Principal Maximum of the Fluorescence Spectrum of Magnesium Phthalocyanine in the Adsorbed State. V. F. Gachkovsky. *Doklady Akad. Nauk S.S.S.R.*, **71**, 509–511 (21st March 1950).

A further examination was made of the fluorescence spectrum of magnesium phthalocyanine, adsorbed from its soln. in ethanol on to magnesium oxide (cf. J.S.D.C., **66**, 557 (Oct. 1950)). The adsorbate was degassed *in vacuo* at various temperatures, and the fluorescence examined after cooling to 20°c. The intensity fell with increasing degassing temp. and became zero at 400°c.; at the same time there was a change in the character of the principal maximum (635–710 mμ.). Thus, after degassing at 300°c. the original broad maximum was replaced by two well defined maxima at 659 mμ. and 697 mμ., and it appeared probable that a number of fluorescent species of varying thermal stability were present in the original adsorbate. After degassing completely and cooling to 20°c., carefully purified ethanol vapour was admitted; the adsorbate immediately became fluorescent with a spectrum maximum at 673 mμ. The procedure was repeated using pure oxygen, and again using pure water vapour to excite the fluorescence. Oxygen gave maxima at 659·3 and 697 mμ., and water a maximum at 679 mμ. The original spectrum could be reproduced by the simultaneous admittance of oxygen, water vapour, and ethanol vapour. In other experiments ethanol was replaced by diethyl ether or acetone with analogous results. A fluorescent adsorbate could not be obtained from the parent phthalocyanine (Mg-free). It is considered to be established that the fluorescent species is a complex formed by the co-ordination at the central Mg of the pigment of an oxygen-containing molecule. The latter may be a solvent molecule, but when the adsorbate is produced without special precautions, complexes will be formed also with oxygen and water which are present as impurities.
A. E. S.

Formation of Tyrosine Melanin—II. G. R. Clemo and F. K. Duxbury. *J.C.S.*, 1795–1800 (July 1950).

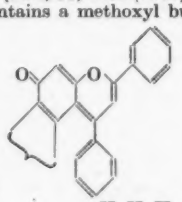
As a contribution to the unsolved problem of the formation of melanin from tyrosine, it is assumed that the indole nucleus of the essential intermediate in the reaction undergoes oxidative coupling at some of the many available centres. Inhibition of melanin formation would be expected if the hydrogen atoms at these centres were replaced by other groups, and, accordingly, 2- and 3-methyl-, 3-methoxy-, and the ethyl ester of *N*-methyltyrosine and 2:4-dihydroxyphenylalanine were treated with tyrosinase and found to yield no melanic pigment. The preparation of these derivatives is described, and the visible and ultra-violet spectra of the various pigments involved are compared and the results discussed. H. H. H.

Carotene as a Pigment for Butter. F. Kieferle, A. Seuss, and H. Kiendl. *Proc. 12th Intern. Dairy Congr.* (Stockholm), **1**, 69–82 (1949).

Actinomycete Pigments. I—Actinorhodin, a Red Antibiotically Active Pigment from Actinomycetes. H. Brockmann, H. Pini, and O. von Plotho. *Chem. Ber.*, **83**, 161–167 (1950).

Pigments of "Dragon's Blood" Resin. I—Dracorubin. (Mrs.) D. A. Collins, F. Haworth, K. Isarasena, and A. Robertson. *J.C.S.*, 1876–1881 (July 1950).

Dracorubin, obtained from commercial specimens of "dragon's blood" resin by extraction with boiling benzene and isolation as picrate, appears to be an anhydro-2:4-diphenylbenzpyranol $C_{32}H_{24}O_5$ of type (I), derived from the 7-hydroxy-2:4-diphenylbenzpyranol, dracorubanol. Contrary to Brockmann and Haase (*Ber.*, **70**, 1733 (1937)) it seems likely that dracorubin contains a methoxyl but not an active carbonyl group.



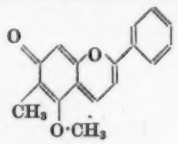
$C_{15}H_9.(O{\cdot}CH_3).2(-O-)$

(I)

H. H. H.

Pigments of "Dragon's Blood" Resin. II—A Synthesis of Dracorhodin. A. Robertson and W. B. Whalley. *J.C.S.*, 1882–1884 (July 1950).

The constitution (I) assigned to dracorhodin by Brockmann and Junge (*Ber.*, **76**, 751 (1943); **77**, 347 (1944)) has been confirmed by a synthesis of the compound starting from acetophenone and 4:6-dihydroxy-2-methoxy-3-methylbenzaldehyde, obtained by hydrolysis of the anil of methyl 2:6-dihydroxy-4-methoxy-3-formyl-5-methylbenzoate with simultaneous decarboxylation of the resulting acid. The two former compounds condense with hydrogen chloride in acetic acid to give 7-hydroxy-5-methoxy-6-methylflavylium chloride, identical with the hydrochloride of natural dracorhodin, which with aqueous sodium acetate or sodium carbonate gave the anhydro base above, identical with the natural compound.



(I)

H. H. H.

Calcium Dichromate. W. H. Hartford, K. A. Lane, and W. A. Meyer. *J. Amer. Chem. Soc.*, **72**, 3353–3356 (Aug. 1950).

An account of an investigation of the system $CaCr_2O_7$–H_2O. Two crystalline hydrates $CaCr_2O_7{,}3\,H_2O$ and $CaCr_2O_7{,}4{\cdot}5\,H_2O$ have been prepared; on heating they decompose partly to $CaCrO_4$ and CrO_3 owing to hydrolysis. There is no evidence of the existence of anhydrous $CaCr_2O_7$ as a pure crystalline phase. At 500°c. there is loss of O_2 to give a mixture of Cr_2O_3 and $CaCrO_4$, which loses O_2 at 1100–1200°c. to form $CaCr_2O_4$.
C. O. C.

White Lead by Electrolysis. I—Preliminary Investigation of a Non-diaphragm Process. A. Venkateswarlu. *J. Sci. Ind. Res.* (India), **9B**, (3), 67–69 (1950): *Chem. Abs.*, **44**, 6749 (10th Aug. 1950).

White lead of composition $2\,PbCO_3{,}Pb(OH)_2$ is obtained electrolytically in a non-diaphragm single-fluid cell, with sheet-Pb electrodes, a bath containing $NaHCO_3$ (1 part), Na_2CO_3 (2), and sodium acetate (10), and a current density of 0·0093–0·016 amp./sq. in.
C. O. C.

PATENTS

Cyanoacetamido Colour Couplers. I. F. Salminen, A. Weissberger, and Eastman Kodak Co. *U.S.P.* 2,507,180.

Compounds of formula $HO{\cdot}R{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$ (R = an aromatic nucleus or system the position in which *ortho* to the OH is either unsubst. or subst. with a replaceable group, e.g. Cl) yield blue to purple, grey to blue–green, and grey to purple images when treated with primary aromatic amino developers.
C. O. C.

***NN'*-Hydrocarbon-substituted *β*-Aminoacrylamide Colour Couplers.** R. M. Leekley and Du Pont. *U.S.P.* 2,507,110.

Compounds of formula $R^1{\cdot}NR^2{\cdot}CAr{:}CH{\cdot}CO{\cdot}NH{\cdot}R^3$ (R^1 = hydrocarbon; R^2 = H, acyl, or hydrocarbon; R^3 = an aromatic hydrocarbon nucleus) are colour couplers when used with primary aromatic amino developers.
C. O. C.

2-Phenylanthraquinone. R. R. Umhoefer and Buffalo Electro-Chemical Co. Inc. *U.S.P.* 2,499,702.

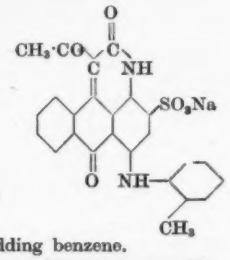
o-(*p'*-Phenylbenzoyl)benzoic acid is heated in conc. H_2SO_4 at 125°c. to produce a sulphonic acid of 2-phenylanthraquinone. This is heated at 200–300°c. in an autoclave with aqueous mineral acid, e.g. a mixture of equal parts by volume of conc. HCl and water, to split off the sulpho group.
R. K. F.

1-Chloro-2-carboxyanthraquinone. M. Scalera and American Cyanamid Co. *U.S.P.* 2,499,003.

1-Nitro-2-carboxyanthraquinone, prepared e.g. by oxidising 1-nitro-2-methylanthraquinone with dichromate in sulphuric acid, is refluxed for 10 hr. with aqueous sodium sulphite containing sodium carbonate. The resulting 1-sulphonic acid is separated by adding sulphuric acid, filtered, and treated in boiling aqueous hydrochloric acid with a solution of sodium chlorate added over 4 hr., when 1-chloro-2-carboxyanthraquinone separates.
R. K. F.

Anthrapyridone Derivatives— Dyes for Cellulose Esters and Ethers. G. W. Seymour, V. S. Salvin, W. D. Jones, and Celanese Corpn. of America. *U.S.P.* 2,501,099.

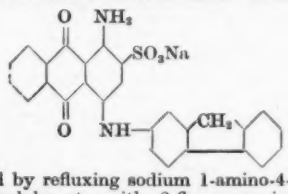
A 1 - amino - 4 - *o* - alkylarylaminoanthraquinone - 2 - sulphonic acid is condensed with ethyl acetoacetate to give light-fast red–violet dyes for dyeing cellulose acetate from a solvent bath. Thus sodium 1-amino-4-(*o*-toluidino)-anthraquinone-2-sulphonate is refluxed with ethyl acetoacetate in presence of sodium acetate, and the resulting dye—



separated by adding benzene. R. K. F.

Fluorenylaminoanthraquinones— Dyes for Animal Fibres and Superpolyamides. C. G. Vogt and General Aniline & Film Corpn. *U.S.P.* 2,499,431.

Water-insoluble blue dyes for wool and nylon are prepared by condensing 1-amino-4-bromoanthraquinone-2-sulphonic acid with a fluoreneamine. Thus the dye—



is prepared by refluxing sodium 1-amino-4-bromoanthraquinone-2-sulphonate with 2-fluoreneamine in aqueous alcohol containing sodium bicarbonate and cuprous chloride for 3 hr. It is separated by distilling off the alcohol and adding HCl, and applied to the fibre as a dispersion. R. K. F.

Green-fluorescent Dyes for Lubricating Oils. R. G. Mastin and Cities Service Oil Co. *U.S.P.* 2,508,617.

The products obtained by treating phenylhydrazine in acetic acid at 100°C. with dianisylideneacetone, anisalcinnamalacetone, and dicinnamalacetone impart green fluorescence to mineral oils. C. O. C.

Cyanine Dyes. General Aniline & Film Corpn., P. Nawiasky, and R. J. Speer. *B.P.* 641,805.

High yields of trimethincyanine dyes containing a substituent on the *meso* carbon atom of the trimethin chain are obtained by treating a *cyclo*ammonium quaternary salt with an alkyl ester of a thioimide in which the N atom bears as a substituent a phenyl radical substituted in the *para* position by a halogen atom. C. O. C.

Cyanine Dyes. General Aniline & Film Corpn. and A. W. Anish. *B.P.* 641,882.

Treating thioethers of *mero*cyanines with an aliphatic or subst. aliphatic compound containing a reactive methylene group yields cyanines containing an additional chromophore unlike that found in trinuclear cyanine dyes. C. O. C.

Heterocyclic Nitrogenous Cyanine Dyes containing a New Group added to their Nitrogen Atom. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,508,324.

Introducing one or two CH_2 groups between a *p*-toluenesulphonate group and a nitrogenous heterocyclic system yields compounds which when used as alkylating or quaternising agents for basic nitrogenous heterocyclic dye intermediates yield cyanine dye salt intermediates. C. O. C.

Carbocyanine Dyes. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,508,325.

In the formation of carbocyanine dyes by condensing 2 mol. of a *cyclo*ammonium quaternary salt, having a reactive CH_3 group in the 2-position to the N atom, with an ortho-ester of a carboxylic acid, use of compounds of formula $R^1{\cdot}CO{\cdot}R^2$ or $R^2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R^4$ (R^1 = an aromatic radical of the benzene series, R^2 and R^4 = Alk or HO·Alk of < 5 C, R^3 = Alk of < 5 C or phenyl) enables condensation to be carried out at a higher temperature and permits it to go more quickly to completion. C. O. C.

Removing Inorganic Salts from Dyes. Chadeloid Corpn. *B.P.* 640,915.

The dye is dissolved to saturation in a solvent for both it and the inorganic salts present, e.g. an ether of diethylene glycol, and filtered; then a thinner comprising a precipitant for the inorganic salts is added, and the liquor finally filtered. As thinner a mixture of 2 vol. of methanol and 1 vol. of toluene per vol. of saturated dye solution is very satisfactory. C. O. C.

Non-dusting Water-soluble Organic Dyes. Allied Chemical & Dye Corpn. *B.P.* 642,338.

Dusting is inhibited by mixing the dye with not $> 6\%$ by weight of a liquid dialkyl phthalate each alkyl group of which has < 5 C. C. O. C.

Fluorescent Material. British Thomson-Houston Co. Ltd. and General Electric Co. *B.P.* 641,212.

A phosphor comprising a matrix of a zirconate of Sr, Ba, or Cd activated with not $> 1\%$ of Bi, Ag, Cu, or Pr is powerfully excited by radiation of 3000–3800 A. to give luminescence free from blue components. C. O. C.

White Pigments. Goodlass Wall & Lead Industries Ltd. and W. E. Green. *B.P.* 641,624.

Lead sulphate is treated in presence of water with a carbonate or silicate of an alkaline-earth metal so as to convert the bulk of the lead from sulphate to carbonate or silicate. The products, while having a much lower lead content than white lead, yield paints having a spreading rate and covering power comparable with those of white lead paints. C. O. C.

White Pigments. Horizons Inc. *B.P.* 641,608.

White pigments are cheaply prepared by treating calcium silicates with acid to produce water-insoluble calcium salts. C. O. C.

Titanium Dioxide. R. M. McKinney and Du Pont. *U.S.P.* 2,507,729.

A rutile TiO_2 nucleating agent is obtained by digesting an alkaline-earth metal titanate at 60–100°C. in presence of a 0·1–1·0 N. concentration of a monobasic acid. C. O. C.

Carbon Black Plant [of Cabot Carbon Ltd., Ellesmere Port, Cheshire]. (I, p. 593.)

Effect of Infra - red and Ultra - violet Radiation on some Colouring Agents for Rubber. M. Déribéré. (XIII, p. 607.)

V— PAINTS; ENAMELS; INKS

Printing Inks from Aqueous Pastes of Pigments and Coloured Varnishes. V. G. Georgievsky and T. V. Polyansky. *Poligraf. Proizvodstvo*, (1), 27–28 (1950): *Chem. Abs.*, **44**, 7070 (10th Aug. 1950).

Review of methods of removing water from printing compositions revealing successful application of previous theoretical work (*J. Phys. Chem.* (*U.S.S.R.*),**1**, 151 (1931)), in which mixing and grinding are combined with heating at 80–100°C. to give satisfactory inks from any pigment combinations and with a saving in time of 60–120 hr. over conventional methods. C. O. C.

PATENTS

Copolymers of *cyclo*Pentadiene. Velsicol Corpn. *B.P.* 640,183.

Copolymers of *cyclo*pentadiene suitable for use in paints and varnishes are prepared by heating *cyclo*pentadiene or its polymers with rosin or its derivatives at 450–600°F. under pressure. E. C.

Modified Melamine–Formaldehyde Resins. Beck, Koller & Co. (England) Ltd., T. S. Hodgins, P. S. Hewett, and A. G. Hovey. *B.P.* 640,203.

Heat- and moisture-convertible melamine resins particularly suitable for use in printing inks are prepared by condensing, in presence of ammonia, melamine (1 mol.) and formaldehyde (3–4 mol.), removing 50% of the latter by vacuum distillation, and treating the residue with a glycol (2–4 mol.), e.g. diethylene glycol or propylene glycol. E. C.

Printing Ink. E. D. Lee, R. J. Schefbauer, and Interchemical Corpn. *U.S.P.* 2,505,866.

A rapid-drying printing ink comprises a pigment dispersed in a solution of a resin in a petroleum hydrocarbon which is slow-drying to non-drying at 20°C. but which volatilises very rapidly at 150°C. The resin used is that fraction of a Utah coal resin which is precipitated on diluting a 25–45% solution of the coal resin in *iso*hexane to 10% concentration with *iso*hexane. C. O. C.

Quick-drying Road-marking Paint. Minnesota Mining & Manufacturing Co. and H. Heltzer. *B.P.* 641,547.

The paint consists of a drying oil varnish, 25–45% by vol. of a brilliantly reflective pigment, a false-bodying agent, preferably magnesium silicate, and 38 lb./gal. of transparent glass beads of average diameter 3–10 mils. C. O. C.

Stable Hot-melt Coating Compositions. W. Horback and Celanese Corpn. of America. *U.S.P.* 2,510,177.

The compositions comprise an active solvent plasticiser (40–100 parts by weight) and cellulose propionate having 0·1–0·5 free hydroxy group per glucose unit and viscosity 10–100 centipoises. C. O. C.

Ethyl Cellulose–Phenol-modified Coumarone–Indene Lacquer for Polystyrene. K. D. Bacon, A. E. Young, and Dow Chemical Co. *U.S.P.* 2,510,851.

A quick-drying moisture-resistant lacquer of good adherence to polystyrene consists of ethyl cellulose, a phenol-modified coumarone–indene resin, and, if desired, a plasticiser. The solvent used is an alcohol or ether–alcohol boiling at 75–140°C. with possible presence of a little of a lower alkyl acetate or other diluent. C. O. C.

Lacquer for Coating Cellulose Propionate Films, etc. A. P. Baruch, R. E. Porzer, and Celanese Corpn. of America. *U.S.P.* 2,510,166.

A smooth, strongly adherent, blush-resistant lacquer which does not attack cellulose propionate surfaces consists of cellulose nitrate of $> 0{\cdot}5$ sec. viscosity dissolved in a mixture of volatile solvents. C. O. C.

Cellulose Nitrate Emulsions. H. C. Phillips and Hercules Powder Co. *U.S.P.* 2,510,834.

Lacquer-in-water emulsions of high solids content are obtained by adding to an aqueous slurry of cellulose nitrate, whilst agitating, a water-immiscible volatile solvent for the cellulose nitrate and an emulsifying agent and homogenising the resultant rough emulsion. C. O. C.

Abrasion-resistant Coatings. Du Pont. (III, p. 596.)

Oil-soluble Metal Salt Compositions. Nuodex Products Co. Inc. (III, p. 596.)

VI— FIBRES; YARNS; FABRICS

Measurement of Friction between Single Fibres. VI— A Theoretical Study of Fibre Friction. B. Olofsson. *Text. Research J.*, 20, 476–480 (July 1950).

The relation $\mu = \mu_0 + aS/N$ (μ = frictional coefficient, N = normal pressure, S = contact area, a = constant, $\mu \to \mu_0$ as $N \to \infty$) fits the results on fibre friction obtained by several workers. It is valid for fibres rubbing against each other and against a different material and for static and kinetic friction. This relation is discussed with reference to current theories of friction, and it is concluded that surface attraction forces are the prime cause of the observed frictional behaviour. A closer surface sticking in the static state is postulated as the reason for the difference between static and kinetic friction. The possibility of the viscous sliding of fibres is discussed. P. C.

Measurement of Friction between Single Fibres. V— Frictional Properties of Viscose Rayon Staple Fibres. B. Olofsson and N. Gralén. *Text. Research J.*, 20, 467–476 (July 1950).

The frictional properties of viscose rayon staple fibres, using the slip-stick method, have been studied. The effect on the frictional characteristics of treatment with oils, finishing agents, and other auxiliary products has been explored. These agents have been classified as (i) low static, low kinetic friction; (ii) high static, low kinetic friction; and (iii) high static, high kinetic friction. Concentration and method of application do not influence the frictional properties. The influence on humidity is small below 85–90% R.H. High humidity and excessive drying increase friction. The dependence of friction on load differs with the treatment. The friction between rayon and wool is influenced by the presence of the scales, and a higher friction in the anti-scale than in the with-scale direction is recorded. A theoretical study of the influence of frictional properties on movement of sliver in drawing frames has been made. The electrical resistance of bundles of fibre after different treatments has been measured. P. C.

Heats of Combustion and Formation of Cellulose and Nitrocellulose (Cellulose Nitrate). R. S. Jessup and E. J. Prosen. *Bur. Stand. J. Res.*, 44, 387–393 (April 1950).

The heats of combustion of cellulose and a series of cellulose nitrates have been measured in a bomb calorimeter. The results have been used to calculate the heats of formation, and an empirical relation is established between the heat of formation and the nitrogen content. W. J. M.

Effect of Deuteration, Oxidation and Hydrogen-bonding on the Infra-red Spectrum of Cellulose. J. W. Rowen and E. K. Plyler. *Bur. Stand. J. Res.*, 44, 313–320 (March 1950).

Regenerated cellulose films were immersed in almost pure deuterium oxide for up to 100 hr. at 52°C. with the object of substituting D for H in the hydroxyl groups. The infra-red spectrum showed little decrease in the 3 μ. region (OH vibration), and only a weak absorption in the 4 μ. region (OD vibration) appeared. This indicates that little exchange has actually occurred, which is contrary to previous reports, in which the exchange was measured by alteration of the density of the heavy water.

The infra-red spectra in the 2–16 μ. region of cellulose nitrate, cellulose oxidised with nitrogen dioxide, alginic acid, and sodium alginate were examined. It was concluded that a strong band at 5·75 μ. is due to the C=O vibration of the carboxyl group, and that the bands at 6·07 and 7·01 μ. are due to nitrogen–oxygen vibrations.

Examination with a high-dispersion prism of the 3 μ. region of a number of cellulose derivatives indicated a minimum at 2·87 μ. in some. The significance of this is discussed, and it is suggested that it may be due to hydrogen-bonding of the type causing dimerisation in alcohols. W. J. M.

Photochemical Degradation of Cellulose in presence of Tungstic Acid. A. Bolliger and N. T. Hinks. *Australian J. Exptl. Med. Sci.*, 27, 569–573 (1949): *Chem. Abs.*, 44, 7057 (10th Aug. 1950).

WO_3 (I) and MoO_3 (II), when finely dispersed on dry filter paper or other polysaccharides, become blue on exposure to light of wavelength 230–390 mμ. Reduction to coloured oxides of lower valency was presumed to be responsible for the change. With I the colour was retained, but with II the colour went in air if light of < 230 mμ. was excluded. Moisture accelerated the rate of colour loss, but re-exposure to light restored it. During 13 days' exposure to sunlight there was no increase of reducing substances in the II–paper system but up to 2% were produced in the I–paper system. One-fourth of the latter was soluble in water. The II–paper became brittle on exposure to sunlight but the I–paper was unaffected. Irradiation of II with a mercury arc lamp for 1 hr. produced negligible amounts of reducing substances. Extended intermittent irradiation gave results comparable to those of sunlight. C. O. C.

Molecular Structure of Wool Keratin. A. C. Goodings. *Text. Research J.*, 20, 454–466 (July 1950).

A critical examination of certain physical properties of keratin, in particular density, together with X-ray data and stereochemical considerations, has led to a structure for keratin which differs from those previously advanced. The main chain repeat of 5·14 A. is explained by a folded configuration containing 2·57 residues or 7 main chain atoms in the repeat, in contradistinction to 3 amino acid residues as postulated by Astbury. The 9·8 A. distance which has previously been regarded as the side chain spacing is considered to be the "backbone" spacing, whilst the average side chain spacing is about 6·1–6·7 A., although no recognisable reflections corresponding to this distance can be seen in the X-ray photograph of α-keratin. The absence of such reflections may be due to a variation in the side chain spacing according to the type of amino acid

present along the main chain. Further details of the axial repeat in α-keratin are discussed. The transformation of α- into β-keratin is considered in the light of the new proposals for the former type and appears to involve a rotation of part of the molecular chain. The contraction of protein fibres and other possible folded configurations are examined. P. C.

Comparative Rain Resistance of Various Wool Fabrics. A. M. Sookne, F. W. Minor, and M. Harris. *Amer. Dyestuff Rep.*, **39**, 548–554 (21st Aug. 1950).

The resistance to penetration and absorption of water of fourteen wool fabrics having widely different structural and physical properties was tested in an artificial 3 in./hr. rain. The effect of a water-repellency treatment on these properties was also investigated. Resistance to penetration increased rapidly with weight and thickness, the knitted samples showing a lower resistance than woven fabrics in the same range of weight. No correlation was observed between penetration in the rain-room and conventional laboratory tests. The absorption of water varied directly with the thickness and approx. inversely with the density of the samples. A good relationship is shown between max. absorption in the rain-room and the modified dynamic absorption test. The water-repellency treatment improved the resistance to penetration and absorption of water in every case. G. E. K.

New Type of Lattice with Large Periods in Silk. O. Kratky, E. Schauenstein, and A. Sekora. *Nature*, **165**, 527–528 (1st April 1950).

A third modification of silk (silk III) has been prepared with a strong 45 A. X-ray reflection. It is suggested that this is due to the planes of the tyrosine residues being oriented in one plane containing the fibre axis. It is reported that every sixteenth amino acid along the peptide chain is a tyrosine residue. W. J. M.

Interatomic Distances and Bond Angles in the Polypeptide Chain of Proteins. R. B. Corey and J. Donohue. *J. Amer. Chem. Soc.*, **72**, 2899, 2990 (July 1950).

Data from recent crystal structure studies of amino acids and peptides are used to derive values for the bond lengths and bond angles of the polypeptide chain of proteins. C. O. C.

Salt Effect in Cellulose Acetate. C. J. Malm, L. J. Tanghe, and G. D. Smith. *Ind. Eng. Chem.*, **42**, 730–734 (April 1950).

The presence of certain multivalent cations in solutions of cellulose acetate gives an enhanced viscosity which is not reflected in an increased strength of the corresponding fibre. This is not desirable. An assessment of the effect has been made, and it is found to be subject to the following variables— nature and amount of salt, pH of solution from which the salt is applied, the solvent, the degree of hydrolysis of the cellulose acetate, and the combined acid content of the cellulose acetate. W. J. M.

Biological Degradation of Soluble Cellulose Derivatives and its Relationship to the Mechanism of Cellulose Hydrolysis. E. T. Reese, R. G. H. Siu, and H. S. Levinson. *J. Bact.*, **59**, 485–497 (1950): *Chem. Abs.*, **44**, 6620 (25th July 1950).

The degree of substitution (D.S.) of soluble cellulose derivatives is a primary factor in determining the resistance of these materials to microbial attack. Presence of a single substituent on each anhydroglucose unit appears to confer immunity. Below this threshold value, increasing the D.S. of the cellulose derivative increases its resistance. Methyl cellulose and hydromethyl cellulose with the high D.S. required for solvation are usually resistant to microbial attack. Carboxymethyl cellulose and hydromethyl cellulose as usually found on the market are readily hydrolysed by cellulolytic fungi. Ability to hydrolyse the 1:4-β-glucoside linkage found in cellulose is not limited to cellulose-decomposing organisms. Non-cellulolytic organisms grown on soluble carboxymethyl cellulose or on hydromethyl cellulose also attack this linkage and produce filtrates having the hydrolytic enzyme. Biological solubilisation of cellulose probably takes place in at least two steps— conversion of the native cellulose molecule into linear anhydroglucose chains and hydrolysis of the 1:4-β-glucosidic linkage to form soluble sugars. C. O. C.

PATENTS

Cellulose for Viscose Manufacture. Rayonier Inc. and R. L. Mitchell. *B.P.* 641,242.

Incorporation of a water-soluble Mn compound into refined cellulose, e.g. 1–100 p.p.m. as Mn, permits great reduction of the time necessary for ageing the xanthated pulp. J. W. B.

Carboxymethyl Cellulose Filaments. Comptoir des Textiles Artificiels. *B.P.* 640,972.

Filaments of good handle and mechanical strength and with little tendency to swell after drying are obtained by extruding an alkaline solution of carboxymethyl cellulose into an acid bath in absence or presence of salts, treating the resulting filaments with solutions of metallic salts to render them insoluble, rinsing thoroughly, then treating with solutions of surface-active cationic agents, and finally drying. C. O. C.

Nylon Filaments. I.C.I. Ltd. *B.P.* 640,582.

Nylon filaments having wool-like crimp and improved dye receptivity are obtained by heating a relaxed, oriented nylon filament, which has been rendered insoluble in solvents, e.g. cresol, in which it was originally soluble, at 10–50°c. below the softening point of the treated filament, until it has shrunk at least 50% in length. In one example filaments are soaked for 16 hr. in 1% aq. NH_4Cl soln., washed, dried, and treated for 15 min. at 150°c. with anhydrous formaldehyde vapour. They are then shrunk about 75% by passing, while relaxed, for 3 sec. over a metal bar heated to 260°c. J. W. B.

Nylon of Low Thermal Extensibility. J. B. Miles and Du Pont. *U.S.P.* 2,509,740.

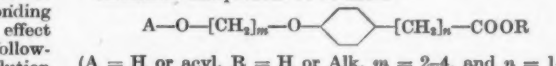
Nylon especially suitable for tyre cords and other fabrics requiring yarns of high tenacity is obtained by treating nylon with a swelling agent while it is being drawn to a residual elongation not $> 14\%$ and to not $< 0{\cdot}5\%$ beyond its completely drawn length. Finally the swelling agent is removed while the yarn is still stretched.

U.S.P. 2,509,741.

Completely drawn nylon while having a stretch of not $< 0{\cdot}5\%$ is heated dry at 100–5°c. below its m.p. The yarn is then cooled while stretched to a temperature at least 5°c. lower than that to which it was heated. At least two of the yarns are then plied and twisted to form a cord, which is then given the same heating and cooling treatment. C. O. C.

Fibre-forming Polymeric Esters. Courtaulds Ltd., F. Reeder, and E. R. Wallsgrove. *B.P.* 641,320.

Aromatic compounds of formula—



(A = H or acyl, R = H or Alk, m = 2–4, and n = 1–4) are autocondensed by heat into polymeric esters suitable for spinning into fibres. J. W. B.

The Rôle of the Electric Double Layer in the Sorption of Acids and Dyes by Wool. P. Alexander and J. A. Kitchener. (VIII, p. 603.)

Quantum Yields of Decomposition Products from the Copolymer of Vinylidene and Vinyl Chloride. J. E. Wilson. (XIII, p. 607.)

Protein Plastics. J. H. Collins. (XIII, p. 607.)

Heat- and Light-stabilised Polyvinyl Chloride Resins. G. P. Mack and Advance Solvents & Chemical Corpn. (XIII, p. 607.)

Plasticising Polymeric Hydrocarbons. F. W. Lord, T. J. Meyrick, L. B. Morgan, and I.C.I. Ltd. (XIII, p. 607.)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Application of Enzymes in Textiles. J. Pfannmuller and A. Noe. *Amer. Dyestuff Rep.*, **39**, P 490–P 496 (24th July 1950).

The general properties, mode of action, and optimum conditions of use of enzymes are described, with particular reference to the use of amylases in desizing starch-sized fabrics and of proteases in the removal of gelatin sizes.

All enzymes are heat-sensitive, are active only within a limited pH range, and are destroyed by certain chemicals, particularly heavy-metal salts. Individual enzymes, however, differ widely in these respects. A number of methods for evaluating commercial enzyme preparations are described in detail. These mostly depend upon determining their starch- or gelatin-liquefying power under rigidly standardised conditions and on actual desizing tests. W. K. R.

Soap and Detergents as affecting Textiles. F. D. Snell. *Amer. Dyestuff Rep.*, **39**, 481–484 (24th July 1950).

The physicochemical mechanisms of wetting and detergency are discussed, and the results of some recent investigations concerning the suspending power of built detergents, the varying detergent efficiency obtained with different soils and different fibres, and the use of built soap–synthetic detergent mixtures are reviewed. W. K. R.

Solubilisation in Alcohol–Soap Micelles. H. B. Klevens. *J. Amer. Chem. Soc.*, **72**, 3581–3586 (Aug. 1950).

Use of long-chain alcohols, from *n*-heptanol to *n*-dodecanol, as additives markedly increases solubilisation of *n*-heptane in potassium *n*-tetradodecanate solutions. They enhance the solubilising power much more than equivalent amounts of soaps of the same chain length. When the polar group on the additive is changed, then for equal chain lengths $COO^- < OH < NH_2 < SH$ in enhancing solubilisation, probably because of greater penetration into the palisade layer of the soap micelle of the various polar compounds in the same order as the increase in solubilising power. This is in agreement with the attraction of these polar groups for the water layer due to its high dipole moment. C. O. C.

Suspending Power of Detergent Solutions. I— Pure Soaps. A. S. Weatherburn, G. R. F. Rose, and C. H. Bayley. *Canadian J. Res.*, **28 F**, 213–225 (June 1950).

The suspending powers (S.P.) of the sodium soaps of pure lauric, myristic, palmitic, stearic, and oleic acids were assessed by measuring photometrically their efficiency in preventing soil deposition on to cotton cloth shaken in dispersions of various carbon black and other soils in the soap solution. S.P. increased rapidly with increasing soap concentration and reached a maximum at relatively low concentrations (ca. 0·02–0·05%), after which it either remained constant or decreased slightly. Different results were obtained with the various soils, both in the magnitude of the indicated S.P. and in the shape of the curve obtained by plotting S.P. against soap concentration. With carbon black soils the indicated S.P. for a given soap generally increased with increasing particle size and decreasing structure of the carbon. Using only one carbon black soil, only slight differences were found in the S.P. of sodium myristate, palmitate, and stearate, all of which were higher than that of the laurate. With increasing temperature (25–80°C.) S.P. of the C_{12} and C_{14} soaps decreased whilst those of the C_{16} and C_{18} soaps increased, and the S.P. of sodium oleate remained substantially constant. W. K. R.

Effect of Electrolytes upon Solubilisation of Hydrocarbons and Polar Compounds. H. B. Klevens. *J. Amer. Chem. Soc.*, **72**, 3780–3785 (Aug. 1950).

Addition of KCl to 0·32 N. potassium tetradodecanate (KC_{14}) solution enhances solubility of *n*-heptane and decreases that of *n*-octanol. With 0·05 N-KC_{14}–KCl soln., solubilities of both polar and non-polar compounds increase. However, after the initial increase up to about 0·50 N-KCl, solubility of the alcohol again decreases. Even though the critical micelle concentration of a soap depends only on the equivalent concentration of the ion opposite in charge to that of the colloidal electrolyte, the nature of both anion and cation affects solubilisation. Thus, in the solubilisation of *n*-heptane for equivalent concentrations of additive, $KCl > K_2SO_4 > K_4Fe(CN)_6$, whereas the reverse order holds when *n*-octanol is solubilised. However, these latter data are additional proof of two loci of solubilisation, one in the hydrocarbon centre of the micelle, the other in the palisade layer in the region occupied by the soap molecules. As the chain length of the solubilised alcohol is increased, there is gradual transition from polar to non-polar type of solubilisation. Addition of very small amounts of long-chain alcohols to soap–salt systems results in formation of very viscous, almost gel-like, systems. Maximum viscosities always occur at concentrations of alcohol below the limit of solubilisation (as indicated by turbidity). C. O. C.

Influence of Sodium Carboxymethyl Cellulose on the Suspending Power of Built Soap Solutions. C. H. Bayley and A. S. Weatherburn. *Text. Research J.*, **20**, 510–513 (July 1950).

Alkaline builders such as sodium carbonate, metasilicate, and orthosilicate reduce the suspending power of soap solutions, but the addition of carboxymethyl cellulose to such built soap solutions compensates to a considerable extent although never completely the loss in suspending power. Maximum improvement was obtained with 5% agent calc. on the weight of soap used. P. C.

Sorption of Soap by Textile Fibres. A. S. Weatherburn, G. R. F. Rose, and C. H. Bayley. *Canadian J. Res.*, **28 F**, 51–61 (March 1950).

The sorption of the sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids from aqueous solutions by textile fibres has been measured. The sorption was found to increase in the following order— cotton, nylon (dull and bright), acetate rayon (dull and bright), bright viscose rayon, dull viscose rayon, and wool. The sorption of fatty acids showed a distinct maximum with variation in chain length, which occurred at myristic acid. The sorption of sodium oleate corresponds to the sorption of C_{14}–C_{16} saturated fatty acid. The alkali sorption was also measured. Suppression of hydrolysis by addition of alkali decreased the sorption of fatty acid in all cases. It is concluded that the sorption process is complicated and involves the independent sorption of "neutral soap", free acid, and hydrolytic alkali. W. J. M.

Some Physical-Chemical Aspects of Cotton Detergency— Cationic Adsorption and Exchange as shown by Radiocalcium Tracer Studies. J. M. Lambert. *Ind. Eng. Chem.*, **42**, 1394–1398 (July 1950).

The important rôle of adsorption in detergency is illustrated by experimental data on the adsorption of surface-active agents on cotton. A radioisotope tracer method is described for measuring the adsorption and exchange of calcium on cotton in laboratory wash tests simulating hard-water laundering. Results obtained with six detergents in multicycle wash tests are presented. Varying amounts of calcium are adsorbed, increasing with each wash and depending on the detergent and on the condition of the cloth, adsorption being much greater on used than on new cotton. It is also shown that extensive exchange of calcium takes place in each wash cycle. W. K. R.

Simplified Methods of Bleaching Wood Pulp. B. S. Zhevaikin. *Bumazh. Prom.*, **24**, (4), 37–39 (1949): *Chem. Abs.*, **44**, 6623 (25th July 1950).

Writing paper containing 25% bleached cellulose together with wood pulp bleached by Zn or Na dithionites (hydrosulphites) in the beater showed improvement with regard to loss in strength during aging as compared with paper containing 50% bleached sulphite pulp and allowed a saving of 5–10% in cost. Similarly, printing paper containing 10–15% of dithionite-bleached wood pulp showed improved aging characteristics as compared with paper made from 100% bleached pulp. The results are attributed to the dithionite acting as an antichlor. C. O. C.

Harris Colour-stripping Process. M. D. Ewing. *Textile Ind.*, **114**, (6), 99, 100 (1950): *Chem. Abs.*, **44**, 6627 (25th July 1950).

An account of the effective stripping of rags, etc. without seriously damaging the fibres, the latter being protected by chemically replacing their disulphide links by a completely stable linkage. Advantages and limitations of the process are noted. C. O. C.

PATENTS

Dry Scouring of Greasy Wool or Wool Wastes. P. Townsend. *B.P.* 641,678.

The material is opened up and simultaneously treated with powdered dehydrated kaolin, suitable apparatus being described. C. O. C.

Cleansing Raw Wool or Sheepskins. M. Levin. *U.S.P.* 2,508,406.

The material is treated with a mixture of sulphuric acid, a ketone which inhibits ionisation of sulphuric acid, e.g. methyl ethyl ketone, and not > 20% of water. Excess liquor is then removed, the material is heated in two stages, firstly to remove the ketone and secondly, at a higher temperature, to carbonise vegetable matter present, and finally the material is crushed and the charred vegetable matter removed. The grease and/or tar or paint present in the material is dissolved out into the treating bath by the ketone.

U.S.P. 2,508,407.

Hydrochloric acid is used instead of sulphuric acid, and the mixture contains not > 8% of water. C. O. C.

Sorption of Sodium Silicates and Silica Sols by Cellulose Fibres. R. C. Merrill and R. W. Spencer. (X, p. 604.)

Some Physical-Chemical Aspects of Cotton Detergency— Limitations of Present Laboratory Testing Methods. J. M. Lambert and H. L. Sanders. (XIV, p. 608.)

VIII— DYEING

Practical Aspects of High-temperature Dyeing. R. D. Robinson and C. L. Zimmerman. *Amer. Dyestuff Rep.*, **39**, P 250–P 256 (17th April 1950).

The development of high-temperature dyeing technique is described from laboratory experiment with mercury seals to the full-scale plant for continuous dyeing at a speed of 25 yd./min. The latter uses mechanical sealing rolls to hold back a pressure of 50 lb./sq. in., and the dye is fed into the machine by padding the fabric before its entry. The rate of dyeing is increased very greatly. In one case a 60-sec. dyeing at 275°F. showed better penetration than 2 hr. at 200°F. The decomposition of the dyes at elevated temperatures was studied, and some were found unsuitable. With the exception of acetate rayon the fibres used showed no degradation at the temperatures used for the short period of dyeing. Dyeings have been made on the following fibres— wool, cotton, viscose, Aralac, cellulose acetate, silk, nylon, immunised cotton, goat hair, cashmere, rabbit fur, linen, alpaca, mohair, and polyacrylonitrile (Orlon). The highly resistant Orlon shows considerable promise by this method. W. J. M.

Kinetics of Wool Dyeing. I— Simple Acid Dyes. P. Alexander and R. F. Hudson. *Text. Research J.*, **20**, 481–491 (July 1950).

Two processes can control the rate of dyeing wool with Acid Orange II— (i) diffusion of dye through an unstirred film of liquid, and (ii) diffusion through the fibre. For low dye concentrations (i) is the slower process whatever the degree of agitation. At higher concentrations (ii) becomes operative when the rate of stirring is increased beyond the point at which the reaction becomes independent of stirring and the activation energy changes from 5 to 13 kg.cal. per mole. At high concentrations diffusion of dye through the fibre proceeds from a saturated film on the fibre surface, whilst at low concentrations diffusion through the unstirred film is operative. Both processes can be treated quantitatively, in contrast to the process that occurs at intermediate concentrations. Dye is not transported through pores, but rather diffusion occurs by displacement of peptide molecules in the swollen gel-like fibre. P. C.

The Rôle of the Electric Double Layer in the Sorption of Acids and Dyes by Wool. P. Alexander and J. A. Kitchener. *Text. Research J.*, **20**, 203–214 (April 1950).

The theories of adsorption of acids and dyes by wool are critically discussed with continual reference to the nature of the electrical double layer under the appropriate conditions. It is shown that the adsorption may be readily understood from the known properties of the double layer. Dye ions may be taken up as gegenions to the strongly adsorbed proton under acid conditions. When this occurs the adsorption follows the theoretically simple Langmuir type of adsorption on specific sites. Under neutral dyeing conditions they may act as leading ions adsorbed by non-Coulombic forces, under which circumstances they are adsorbed on non-specific sites. The adsorption follows a Freundlich type of isotherm and the behaviour becomes similar to that of the direct dyeing of cotton. The absence of activity coefficient data for dye solutions increases the difficulties of theoretical treatments.

W. J. M.

Influence of Tension on Lustre and Dyeing of Viscose Rayon Yarn. G. Quintelier and L. Hermanne. *Rayonne*, **6**, (1), 47–50 (1950): *J. Textile Inst.*, **41**, A 297–A 298 (June 1950).

The results are presented of a series of experiments on the effect of tension on the lustre and on the depth of dyed shade of viscose rayon yarns. It is found that a "shiner" is not caused directly by tension but by the position it takes in the fabric under the influence of tension; a yarn dyed under tension is lighter in shade than a yarn dyed without tension, irrespective of whether it is dried with or without tension. A brief interpretation of the results is given.

C. J. W. H.

Colouring Glass Fibre. W. Garner. *British Rayon & Silk J.*, **26**, 74–75, 82 (Jan. 1950): *J. Textile Inst.*, **41**, A 195 (April 1950).

The colouring of glass fibres may be carried out by (*a*) colouring the melt before spinning, or (*b*) superficial coating of the fibre. The first method is impracticable for textile purposes. Some patented methods for applying colour to glass fibres by the second method are discussed. The modern techniques attempt to produce a continuous film round the fibre of some material which will take the dye. C. J. W. H.

Dyes and their Application to Paper. F. A. Craig. *Proc. Tech. Sect. British Paper & Board Makers' Assocn.*, **31**, 81–105 (Feb. 1950).

The classification of dyes for colouring paper, their properties and uses, the selection of dyes and mordants, and the identification of dyes in paper are discussed, together with colour room equipment, layout of beaters and chests, method of adding dyes, matching shades in preliminary trials and on the machine, making colour changes, silurian papers, and common colour defects in paper. S. V. S.

IX— PRINTING

Indanthren Type of Steamer. Anon. *Textile Manuf.*, **76**, 31–33 (Jan. 1950).

The Indanthren type of steamer, among other advantages, shows economy of space, time, and steam, and has found favour in the smaller type of steaming unit. However, considerable experience is necessary for its successful use. The main faults and their rectification are discussed, and advice is given on the precautions required in using this type of steamer. The main factors involved are the prevention of channelling of the steam by even packing and tensioning of the goods and the use of sufficiently saturated steam. Attention must be paid to the possibility of improving printing by alteration in the printing paste recipe. The small volume and the ease of displacement of air make the Indanthren type of steamer particularly suitable for vat dye printing. W. J. M.

Coloured Photographic Images by Electrolysis or Electrosynthesis. J. Rzymkowski. *Science et Ind. phot.*, **21**, 86–88 (1950): *Chem. Abs.*, **44**, 6754 (10th Aug. 1950).

A soln. containing phenol and nitrothymol, nitrocresol, or nitronaphthol was electrolytically reduced to produce a reduced indophenol. This functions as an active developing agent, giving rise to an indophenol dye image which is deposited along with the silver. Details are given for the electrolytic reduction of a mixture of *p*-nitrophenol and ethyl acetoacetate, producing the leuco azomethine, which yields a brown azomethine dye when used as a developer. C. O. C.

PATENTS

Silk-screen Printing Paste for Production of Platinum, Silver, or Gold Effects on Heat-resisting Bases. F. E. Kerridge, C. S. Couper, and Johnson, Matthey & Co. Ltd. *B.P.* 641,205.

A silk-screen printing paste for preparing transfers or for direct application to a base resistant to heating to at

least 400°C. comprises Pt powder or a mixture of Pt and/or Pd powder with Au powder, a vehicle, and a volatile solid which is insoluble in the vehicle and which does not carbonise when the base is fired.

B.P. 641,525.

A similar paste contains Au powder as the only pigment. C. O. C.

Stabilised Aryl Diazo-*N*-sulphonate Light-sensitive Material. General Aniline & Film Corpn., W. H. von Glahn, and M. K. Reichel. *B.P.* 641,276.

The stability and printing speed of a light-sensitive heat-developable layer containing a diazo-*N*-sulphonated derivative of a *p*-phenylenediamine is increased by adding an alkali-metal bisulphite and a ketone, ketonic acid, or aromatic aldehyde which forms an addition product with bisulphites. C. O. C.

Aftertreatment of Diazotype Prints. General Aniline & Film Corpn. and S. C. Slifkin. *B.P.* 641,323.

Dry- or semi-wet-developed diazotype prints are stabilised to discoloration on exposure to light without causing undesirable change in their colour by washing them in an aqueous solution (pH 5–7) of a water-soluble orthophosphate of formula $MR^1R^2PO_4$ (M = alkali metal or NH_4; R^1 and R^2 = H or C_{1-3} Alk). C. O. C.

Photographic Dye Images. A. K. Soper and Kodak Ltd. *B.P.* 641,355.

Multicolour Photographic Images. J. H. Coote and A. S. J. Austin. *B.P.* 640,979.

Direct Positive Photographs using Colour Developers. D. B. Glass, F. A. Richey, and Eastman Kodak Co. *U.S.P.* 2,507,154.

X—SIZING AND FINISHING

Mercerisation of Cellulose by Caustic Soda. E. Calvet. *Mém. Services chim. État* (Paris), **34**, 163–177 (1948): *Chem. Abs.*, **44**, 7064 (10th Aug. 1950).

Heat of wetting (exothermic) of cellulose with mercerising lye increases from 3 g.cal./g. at < 1·5 N. to 59 g.cal./g. at 12·44 N. with plateaus of 23 g.cal./g. at 4·3–5·3 N. and 26·4 g.cal./g. at 5·7–6·8 N. These plateaus are ascribed to an endothermic transformation of mercerisation at these points. Mercerised cellulose and viscose rayons give essentially linear plots of heat of wetting against concentration of caustic soda. All this work was done on cellulose containing 3·5% moisture. Comparison of heats of wetting of mercerised and non-mercerised cellulose in 5·262 N-NaOH indicates an endothermic heat of mercerisation of 3·8 g.cal./g. Absorption of NaOH by cellulose is a reversible phenomenon providing mercerising concentration is not attained. Use of interferometric diffusion techniques indicates—unmercerised ramie absorbs NaOH proportionately to alkali concn., with a value of 0·68 $NaOH/C_6H_{10}O_5$ at 15°C.; mercerised ramie absorbs NaOH with no effect of concn. between 2 and 5 N-NaOH, with a value of 0·65–0·70 $NaOH/C_6H_{10}O_5$. At 40°C. both mercerised and non-mercerised ramies absorb NaOH equally and less than at 15°C. C. O. C.

Factors affecting the Relaxation Shrinkage of Knit Underwear Tubing. L. I. Weiner. *Amer. Dyestuff Rep.*, **39**, 241–248 (17th April 1950).

The effect of knitting and finishing variables in shrinkage of typical knit cotton underwear tubing is studied. A major portion of potential shrinkage is introduced in the knitting operation. Possible improvements in this process are described. Conventional wet finishing and drying gives a fabric with less potential length shrinkage than grey fabric. Potential width shrinkage is removed in wet processing, while the improvements in length shrinkage produced by improved knitting are maintained. Calendering may be adjusted to increase or decrease potential shrinkage according to the adjustment of the frames used. In this way it is possible to adjust the fabric for balanced shrinking. Using the methods described it is possible to produce a balanced shrinkage in length and width superior to that produced by normal manufacturing methods. W. J. M.

Improvement of the Resistance of Cotton Cloth to Soiling. W. P. Utermohlen, Jr. *Amer. Dyestuff Rep.*, **39**, P 262–P 264 (17th April 1950).

The resistance of cotton cloth to soil acquisition and the ease of soil removal have been studied on cloths which had been treated physically and chemically in a number of ways. It was found that partial acetylation was particularly effective and, in general, alteration of the electrical charge of the fibre by introducing acidic groups increased soiling resistance and ease of cleaning. Improvement was noticed with the majority of softeners, polycarboxylic resin, mercerisation, partial carboxymethylation, and partial acetylation. No definite effect was noticed with starch, some softeners, and some resins (mostly condensation type). Hydrophobic finishes and most resins (especially vinyl type) reduced the soiling resistance. W. J. M.

Sorption of Sodium Silicates and Silica Sols by Cellulose Fibres. R. C. Merrill and R. W. Spencer. *Ind. Eng. Chem.*, **42**, 744–747 (April 1950).

The sorption isotherms of alkali and silica from sodium metasilicate, $Na_2O,3{\cdot}37\ SiO_2$, N-Sol A, and a sulphuric acid-treated silica sol have been measured at 25°C. for four types of paper pulp. The isotherms are of the Freundlich type. Alkali is usually adsorbed to a greater extent than the silica. The discussion includes consideration of possible bonding methods. Practical implications are discussed. W. J. M.

Zirconium Compounds in Water-repellents for Fabrics. W. B. Blumenthal. *Ind. Eng. Chem.*, **42**, 640–642 (April 1950).

The use of zirconium salts in water-repellent treatment is reviewed briefly. It is reported that zirconium salts alone render textiles somewhat water-repellent, but when used with soaps and wax emulsions a very high-quality water-repellence results. The finish is not fast to laundering or dry cleaning, but may be improved by the addition of a salt with a strongly acid hydrolysis. The wax emulsion Ceremul A in combination with zirconium salts was found particularly effective. It is noted that this wax alone confers little water-repellence on the fabric, and it must be inferred that the zirconium fixes the wax to the fibre. W. J. M.

Effectiveness of Repellents applied to Clothing for Protection against Salt-marsh Mosquitoes. C. N. Smith and D. Burnett. *J. Econ. Entomol.*, **42**, 439–444 (1949): *Chem. Abs.*, **44**, 6567–6569 (25th July 1950).

The results obtained by the use of approx. 3400 compounds against *Aedes ægypti* in the laboratory showed that about 900 of them prevented < 5 bites/min. for at least 10 days after treatment of the fabric. 375 of these cpd. were then given field tests chiefly against *A. tæniorhynchus* (and sometimes *A. sollicitans*), and the results of these tests are given. Outstanding repellents were *N-cyclo*hexyl-2-(butoxyethoxy)acetamide, 2-ethyl-2-butyl-1:3-propanediol, 2-ethylhexyl diethylene glycol monoether, *N*-(mixed monoamyl)imide of 3:6-*endo*methylene-4-*cyclo*hexene-1:2-dicarboxylic acid, *iso*bornyl 4-morpholineacetate, and hendecylenic acid. C. O. C.

PATENTS

Reducing the Brittleness of Natural Fibres. British Brush Manufacturers' Research Assocn. Ltd., D. Emmott, and C. S. Whewell. *B.P.* 640,985.

The brittleness of such fibres as coir is reduced by first softening them by treatment with an alkaline solution in absence or presence of an oxidising agent, then impregnating with the components of a synthetic resin, and finally heat-curing. The treated fibres are much more easily handled and can be machine-punched during brush making without undue breaking. C. O. C.

Permanently Set Hard-twist Wool Yarn. R. J. Jackson and Bigelow-Sanford Carpet Co. Inc. *U.S.P.* 2,509,347, *U.S.P.* 2,509,348.

Hard-twisted yarn is formed into hanks free from tension so that the yarn coils upon itself and kinks. The kinked yarn is wetted and then treated with saturated steam at 5–40 lb./sq. in. until the twists and kinks in the yarn are

set. Pile fabrics woven from such yarns have improved texture, very few, if any, untwisted tufts, increased lustre imparting a pearly appearance, and a set resistant to wetting and shampooing. C. O. C.

Axminster Pile Fabric. H. A. Reinhardt, C. R. Johnson, and Bigelow-Sanford Carpet Co. Inc. *U.S.P.* 2,509,351, *U.S.P.* 2,509,352.

Hard-twisted yarns containing permanent kinks are wetted and then dried under sufficient tension to straighten out the kinks. The yarn is then used for the pile of an Axminster fabric, after which the pile is wetted and dried, thus restoring the tendency of the pile yarn to kink and softening and swelling the tufts of pile while retaining their twist. C. O. C.

Coating Sheet Material with Polyethylene Compositions. I.C.I. Ltd. and W. E. F. Gates. *B.P.* 641,568.

Coatings of high gloss, high resistance to moisture and chemicals, and high mechanical strength may be obtained on weak materials, e.g. thin paper, by bringing a film of high-grade polyethylene composition into contact with a lower-grade polyethylene composition coating on the sheet material, and bonding the film and coating together by heat and pressure. C. O. C.

Textile Fabric coated with Ethyl Cellulose. W. W. Koch and Hercules Powder Co. *U.S.P.* 2,507,107.

Good adhesive coatings which do not embrittle on aging are obtained by applying (1) a "wetting coat", which is a highly plasticised cellulose ether composition; (2) a "toughening coat", which is a similar composition but less highly plasticised; and (3) a "sealing coat", which comprises a cellulose ether of a substitution type which does not allow the plasticisers in the other two coats to penetrate through it. The first two coats may be pigmented, and the third coat may contain a flatting agent. C. O. C.

Coating by Film-transfer. Sylvania Industrial Corpn. *B.P.* 641,412.

A thin film of a polyvinyl resin and a thermoplastic thermosetting resin which will polymerise to an infusible non-thermoplastic state, e.g. melamine–formaldehyde resin (30 parts by wt.) and polyvinyl acetate methylal (70), is applied, e.g. from a 30% solution in dioxan, to a non-fibrous non-resinous backing surface, e.g. a metal band, and dried at a non-curing temperature. Transfer to the requisite surface, e.g. nylon material, is effected by heat and pressure, the backing surface being subsequently removed and the film finally cured at a higher temperature. J. W. B.

Felt Hats. Oldham & Fogg Ltd., J. A. Oldham, and E. Oldham. *B.P.* 640,881.

If the surface of the felt is given a high finish it may be spray-coated with a powdered fibre and then polished by light brushing or rubbing, which may include use of a very fine abrasive surface. C. O. C.

Comparative Rain Resistance of Various Wool Fabrics. A. M. Sookne, F. W. Minor, and M. Harris. (VI, p. 601.)

Action of Formaldehyde on Proteins. R. D. Haworth, R. MacGillivray, and D. H. Peacock. (XII, p. 606.)

Continuous Vulcanisation Processes. W. H. Reece. (XIII, p. 607.)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Sizing Paper with Paraffin Wax. A. I. Perelygina. *Bumazh. Prom.*, **24**, (4), 16–19 (1949): *Chem. Abs.*, **44**, 6623 (25th July 1950).

Because of the adverse effects of rosin on paper and because of lack of rosin, sizing with paraffin wax was developed. A typical size recipe was 100 kg. paraffin wax, 20 kg. stearin, 10 kg. gelatin, and 8 kg. $Na_2B_4O_7$. The final emulsion contained 25–30 g. solids per litre and had pH 8·5–9·5. Stability of the emulsion increased at higher pH, and coagulation occurred at lower pH. Care had to be taken when emulsifying to have the solutions of borax and gelatin at the same temperature as the paraffin wax–stearin melt. Paraffin wax size can be used in conjunction with rosin size (0·5% paraffin wax on dry weight of fibre) and a fourfold reduction in rosin size required (from 2·0 to 0·5%) can be achieved in this way. C. O. C.

High-rosin Paraffin Wax Size for Paper. E. M. Berkman. *Bumazh. Prom.*, **24**, (5), 15–18 (1949): *Chem. Abs.*, **44**, 6623 (25th July 1950).

Increased degree of sizing for the same amount of size was obtained in the order—"white" rosin size, rosin–paraffin wax size, high-rosin size, high-rosin–paraffin wax size. Optimum rosin : paraffin wax ratio was about 60 : 40. Optimum fold properties were obtained from high-rosin–paraffin wax sized paper when the wax content of the size was 60%; optimum breaking length [*sic*] was obtained at 50% wax content. C. O. C.

Desizing of Paper. A. P. Petrov. *Bumazh. Prom.*, **24**, (5), 10–15 (1949): *Chem. Abs.*, **44**, 6623 (25th July 1950).

Desizing of paper after manufacture can be caused by sunlight, electrical discharges, or certain chemicals. The dependence of the degree of sizing of paper on time is summarised; a drop of perhaps 40% in sizing value occurs in 1–5 days, and then the degree of sizing rises slowly until, after 75 days, the initial value has been regained. The recovery in sizing increases with the amount of alum used in the beater. C. O. C.

Interaction of Nitrocellulose with some Solvents and Non-solvents by the Light-scattering Method. R. H. Blaker and R. M. Badger. *J. Amer. Chem. Soc.*, **72**, 3129–3132 (July 1950).

The thermodynamic interaction between cellulose nitrate and several solvents and non-solvents has been investigated by light-scattering observations on acetone solutions of cellulose nitrate to which the substance in question was added. *n*-Butyl acetate, diethyl phthalate, water, ligroin, and *sec.*-butyl chloride were all selectively adsorbed on cellulose nitrate. An expression is given for the activity of cellulose nitrate as a function of its concentration and of the solvent added. C. O. C.

Pyridinium Salts of Cellulose Acetate–Chloroacetate. C. J. Malm, J. W. Mench, R. F. Williams, Jr., and G. D. Hiatt. *Ind. Eng. Chem.*, **42**, 1547–1550 (August 1950).

The preparation of cellulose acetate–chloroacetates by a variety of procedures is described, and properties and methods of analysis are given, with a table showing composition of starting materials and products obtainable by each of the procedures. It was found that these products react, substantially to completion, with tertiary amines (e.g. pyridine) to give quaternary ammonium salts, a large number of which are water-soluble, but then hydrolyse readily with regeneration of cellulose acetate and liberation of *N*-carboxymethylpyridinium chloride; the pyridinium salt of a cellulose acetate–*β*-chloropropionate, however, is more stable to hydrolysis than the *α*-betaine compounds. There are 25 references. H. H. H.

PATENTS

Washing Paper Pulp to remove Colouring Matter. C. E. Libby. *U.S.P.* 2,502,330.

Better-coloured pulp is obtained by washing it between digesting and bleaching with an aqueous solution containing a molecularly dehydrated alkali-metal phosphate, e.g. sodium hexametaphosphate. C. O. C.

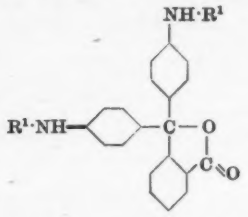
Loading Paper Fibres with Organopolysiloxane-coated Clay. M. M. Safford and General Electric Co. *U.S.P.* 2,510,661.

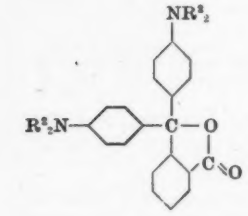
Water-repellent paper is obtained if a paste of (*a*) a finely divided inorganic filler, the particles of which are coated with a thin water-repellent film of organopolysiloxane (obtained by treating the filler with the vapour of a methylchlorosilane or an azeotropic mixture of trimethylchlorosilane and $SiCl_4$), and (*b*) a water-miscible organic liquid is added to the aqueous slurry of the stock before the slurry is beaten. C. O. C.

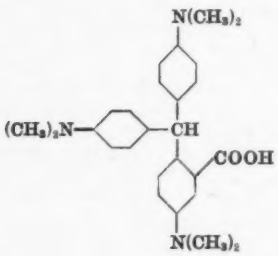
Pressure-sensitive Record Material. B. K. Green and National Cash Register Co. *U.S.P.* 2,505,472–89.

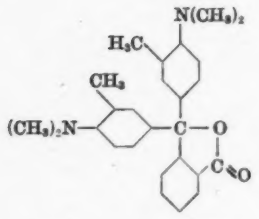
A pressure-sensitive record material which marks only under pressure is obtained by coating paper or the like with two or more substances which in absence of an ionising liquid form a colour when they are brought into adsorption contact with one another. They are insulated from one another by a solid substance, e.g. casein or methyl cellulose, which on application of local pressure is ruptured at

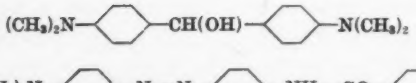
the place where the pressure is applied, thus bringing the colour formers into contact with one another. One of the colour formers is a finely divided inorganic material, e.g. kaolin, which causes a colour change in certain organic compounds when they come into contact with it. These organic compounds have one of the formulæ—

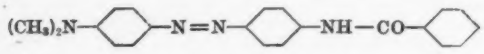


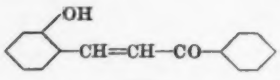


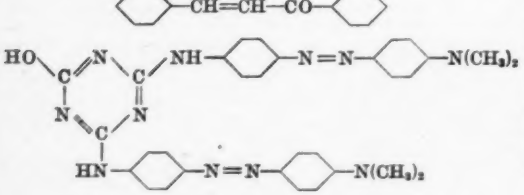


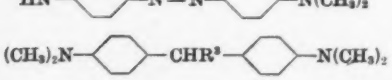












(R^1 = CH_3 or C_2H_5; R^2 = CH_3, C_2H_5, or n-C_3H_7; R^3 = OH or O·CH_3).

C. O. C.

Cellulose Propionate Films. British Celanese Ltd. *B.P.* 638,531.

Flexible films of good strength are obtained by evaporating a solution of cellulose propionate containing < 0·3 hydroxyl group per glucoside unit in a mixture of an aromatic hydrocarbon and an aliphatic ketone, e.g. 75% benzene and 25% acetone. W. G. C.

Clay-coated Paper. A. D. Wilson and S. D. Warren Co. *U.S.P.* 2,500,972.

Reduction in the amount of adhesive needed in clay coatings for paper is obtained if the usual purified clay as it comes from the filter press after slurrying, flocculating, and filter-pressing is mixed with a deflocculant, e.g. a soluble pyrophosphate, and then dewatered, if desired, to dryness. C. O. C.

Bleaching or Brightening Webs or Sheets of Pulp or Paper containing Ground Wood Fibres. R. L. McEwen, F. R. Sheldon, and Buffalo Electro-Chemical Co. Inc. *U.S.P.* 2,510,595.

An aqueous solution of a peroxide and a phosphate is used at pH 9·5–11·5. C. O. C.

Coating Paper, etc. Time Inc. *B.P.* 640,575.

Paper or the like is coated with several layers of coating material to form a uniformly distributed composite layer. At least one of the layers is subdivided, the subdivided layers being transferred successively. The first layer to be applied is thicker than subsequent layers, and at least one layer is applied in a direction counter to the motion of the web. The apparatus used comprises means for supporting the web, for supplying at least two series of distributor rollers from a common source, each co-operating with an applicator roll, and for transferring the layer from each series successively to the web. S. V. S.

Coating Paper. C. R. Outterson, B. A. Ford, and Albemarle Paper Manufacturing Co. (I, p. 593.)

Surface Coverings. United Wallpaper Inc. (III, p. 596.)

Dyes and their Application to Paper. F. A. Craig. (VIII, p. 603.)

Coating Sheet Material with Polyethylene Compositions. I.C.I. Ltd. and W. E. F. Gates. (X, p. 605.)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Early History of Tanning. A. Gansser. *Ciba Review*, (81), 2938–2962 (Aug. 1950).

Subjects covered include the principles of tanning, the dressing of raw hides as an early stage of tanning, tanning materials and tools, primitive methods of tanning, the colouring of leather, basic types of leather, and preservation of skins and leather. C. J. W. H.

Supercontraction of Keratin Fibres. I—Shrinkage of Horsehair in Aqueous Sodium Hydroxide. II—Contraction of Alkali-pretreated Horsehair. H. Zahn. *Kolloid-Z.*, **117**, 102–108 (May 1950).

Horsehair is found to supercontract when it is immersed in an unstretched state in N. aqueous sodium hydroxide at 20°C. for 1–2 hr. and aftertreated in boiling water for 10 min. The influence of chemical pretreatment in general, and of 0·1 N. sodium hydroxide in particular, on the magnitude of the supercontraction in different reagents (phenol, sodium bisulphite, baryta, etc.) has been critically investigated. In agreement with Speakman and Whewell (J.S.D.C., **52**, 380 (1936)), alkali pretreatment of horsehair inhibits further contraction in sodium bisulphite, but an appreciable shrinkage was observed on heating in 50% aqueous phenol. The various mechanisms are discussed. H. H. H.

Action of Formaldehyde on Proteins. R. D. Haworth, R. MacGillivray, and D. H. Peacock. *J.C.S.*, 1493–1498 (June 1950).

Amides, such as benzamide and phenylacetamide, react with formaldehyde at pH 10 to give *N*-hydroxymethyl derivatives which condense with β-naphthol or its 6-bromo or 3:6-dibromo derivative. Many proteins behave similarly

with formaldehyde, etc., and analysis of the analogous condensation products for bromine provides a measure of the number of *N*-hydroxymethylamide groups, the results being roughly proportional to the number of amide groups in the protein molecule. It is concluded that, under the alkaline conditions employed, formaldehyde converts some of the amide groups of the protein molecule into *N*-hydroxymethyl derivatives, but that under acidic conditions the formation of *N*-hydroxymethyl derivatives is reduced. H. H. H.

Structure of Synthetic Polypeptides. A. Elliott and E. J. Ambrose. *Nature*, **165**, 921–922 (10th June 1950).

The polarised infra-red spectra of several new synthetic polypeptides have been examined. It has been possible to identify the 1658 cm.$^{-1}$ and the 1629 cm.$^{-1}$ components of the C=O band with the α- and the β-forms respectively of the polypeptide chain. This, with similar treatment of the N–H frequencies, gives a method of distinguishing between the α- and β-forms in amorphous material, yielding a valuable means of studying denaturation. Further infra-red data and X-ray evidence are advanced to show the close relationship between the structure of synthetic polypeptides and that of natural proteins. W. J. M.

PATENT

Light-resistant White Chrome-tanned Leather. American Cyanamid Co. *B.P.* 639,616.

An aromatic sulphonate tanning agent is used in conjunction with a water-soluble methylolmelamine. This results in chrome-tanned leathers of undiminished strength but improved whiteness and light-resistance. In addition it enables high-grade white leather to be produced from skinny, spready hides that are unsuitable for making white chrome leather by other processes. C. O. C.

XIII—RUBBER; RESINS; PLASTICS

Continuous Vulcanisation Processes. W. H. Reece. *Trans. Inst. Rubber Ind.*, **26**, 137–150 (Aug. 1950).

Processes for the continuous vulcanisation of rubber goods, including rubber-proofed cloth, which are in general use, or used commercially or experimentally by some firms, are described in detail, and some comparisons are made with other vulcanisation methods. C. O. C.

Effect of Infra-red and Ultra-violet Radiation on some Colouring Agents for Rubber. M. Déribéré. *Rev. gén. Caoutchouc*, **27**, 343–346 (1950): *Chem. Abs.*, **44**, 7084 (10th Aug. 1950).

Tables give the effects of exposure to infra-red and ultra-violet radiation of vulcanisates made up of crêpe rubber, lithopone, $BaSO_4$, auxiliary agents, and various percentages of individual and mixed Vulcafixe colours (Fr). C. O. C.

Plasticisers for Polyvinyl Chloride. H. Jones, A. Hill, and I. Williamson. *Plastics Inst. Trans.*, **18**, 50–68 (July 1950).

A review of past work on miscibility, viscosity, etc., dealing particularly with the concept of the effectivity of plasticisers. Original data are presented in connection with the latter to indicate how widely plasticisers differ in effectivity and how the value itself can vary according to the precise method of test used; one of the important variables in the latter respect is time. C. O. C.

Quantum Yields of Decomposition Products from the Copolymer of Vinylidene and Vinyl Chloride. J. E. Wilson. *J. Amer. Chem. Soc.*, **72**, 2905–2908 (July 1950).

The rate of evolution of HCl from the solid copolymer is constant over a tenfold range of intensity using 2537 A. light. The yield of HCl is so small that it is questionable whether the discoloration can be attributed to production of coloured systems of conjugated bonds by HCl loss alone. Evolution of another gas, probably H_2O, was observed. C. O. C.

Protein Plastics. J. H. Collins. *Plastics Inst. Trans.*, **18**, 28–49 (July 1950).

Following a brief history of the use of horn, the manufacture and processing of casein plastics are discussed in full and those of casein fibres briefly dealt with. C. O. C.

Melamine Resins. J. Hofton. *Plastics Inst. Trans.*, **18**, 2–6 (July 1950).

A comparison of the more important properties and applications of melamine–formaldehyde resins compared with melamine–urea resins, including application to paper and textiles. C. O. C.

PATENTS

Heat- and Light-stabilised Polyvinyl Chloride Resins. G. P. Mack and Advance Solvents & Chemical Corpn. *U.S.P.* 2,510,035.

An alkaline-earth metal salt (0·5–6·0%) of a substituted-chain aliphatic carboxylic acid of 4–16 C whose α-C atom is not directly attached to an aryl group stabilises polymeric resins containing > 5% Cl to heat and light. C. O. C.

Polyester Plasticiser for Cellulose Nitrate. D. H. Coffey, O. B. Edgar, T. J. Meyrick, J. T. Watts, and I.C.I. Ltd. *B.P.* 640,597.

Cellulose nitrate is plasticised with a polyester from a dibasic acid and a diol, e.g. polyethylene sebacate, modified by reaction with 3–15% of an organic poly*iso*cyanate, e.g. hexamethylene di*iso*cyanate. E. C.

Plasticising Polymeric Hydrocarbons. F. W. Lord, T. J. Meyrick, L. B. Morgan, and I.C.I. Ltd. *B.P.* 640,494.

Polymeric *p*-phenylene-ethylene (the solid polymer obtained by the pyrolysis of *p*-xylene) is infusible and insoluble in common organic solvents. High-boiling aromatic hydrocarbons, e.g. acenaphthene, anthracene, diphenyl, and naphthalene, are excellent plasticisers for this polymer. The plasticised polymer can be made into filaments or films or used in coatings. C. O. C.

Polymeric 2 : 2 : 4-Trimethyltetrahydroquinoline—Stabiliser for Solid Polymers of Unsaturated Organic Compounds. J. B. Arnold, L. J. Dankert, and Dow Chemical Co. *U.S.P.* 2,500,597.

Polyvinyl Chloride Plasticiser. B. F. Goodrich Co. *B.P.* 638,083.

Polymers and copolymers of vinyl chloride are plasticised with an alkyl (> 3 C) ester of *o*-benzoylbenzoic acid, e.g. cetyl *o*-benzoylbenzoate. E. C.

Polyvinyl Chloride Plasticiser. D. H. Coffey, O. B. Edgar, T. J. Meyrick, J. T. Watts, and I.C.I. Ltd. *B.P.* 638,118.

Polyvinyl chloride is plasticised with 20–100% of a modified polyester prepared from a glycol, a dibasic acid, and < 10% of an organic poly*iso*cyanate. E. C.

Polyvinyl Chloride Plasticiser. B. F. Goodrich Co. *B.P.* 638,567.

Polymers and copolymers of vinyl chloride are plasticised with a liquid ester of tetrahydrophthalic acid or a mixture of such esters of m.p. < 30°c. The compounds show improved stability to heat and light. E. C.

Adhesive for Bonding Polyvinyl Chloride. B. B. Chemical Co. Ltd., T. C. Morris, and E. C. Johnson. *B.P.* 638,085.

A latex of a butadiene–acrylonitrile copolymer containing < 8% of a wetting agent and < 8% of a thickener, e.g. ammonium caseinate, is used for bonding polymers and copolymers of vinyl chloride. E. C.

Drying Oils modified with Vinyl Resins. Beck, Koller & Co. (England) Ltd. and R. S. Robinson. *B.P.* 638,835.

A bodied linseed oil, a bodied dehydrated castor oil, or an alkyd resin modified therewith is mixed with styrene or methyl methacrylate and copolymerised at 60°c. in emulsion by adding with stirring to water containing emulsifiers and a polymerisation catalyst, e.g. ammonium persulphate. E. C.

Plasticising Polyvinyl Resins. B. F. Goodrich Co. and F. K. Schoenfeld. *B.P.* 638,570.

Plasticised vinyl resins, e.g. polyvinyl chloride, are obtained in granular form by vigorously stirring a suspension of the powdered resin and the plasticiser in a non-solvent for both, e.g. water, at < 100°c. After absorption of the plasticiser, the solid is filtered and dried, and may then be rapidly consolidated by hot milling. E. C.

Dialkyl Diphenates— Plasticisers for Polyvinyl Compounds and Cellulose Derivatives. H. Steiner, H. S. Boyd-Barrett, J. R. Holker, and Petrocarbon Ltd. *B.P.* 641,832.

Dialkyl esters of diphenic acid (Alk of 1–8 C) whose alkyl radicals may be substituted by one or more halogen atoms have low density and volatility, good stability to heat and light, and fairly good resistance to fire. Used as plasticisers for polyvinyl compounds, cellulose derivatives, and other organic polymers, they impart great flexibility, high elasticity, and high tensile strength. C. O. C.

Mixed Phthalate Esters — Plasticisers. Nopco Chemical Co. *B.P.* 642,039.

The products obtained by esterifying a monoacyl glycol, the acyl being derived from a C_{8-18} aliphatic acid, with a monoalkyl (C_{1-12}) acid phthalate are high-boiling liquids, which may be decolorised almost to water-white, are compatible with most other plasticisers, antioxidants, etc., and may be used in a wide range of plastic compositions. C. O. C.

Alkyd–Melamine Resin Coating Compositions. M. J. Scott, F. J. Hahn, and Monsanto Chemical Co. *U.S.P.* 2,508,876.

Alkyd resins modified with the condensate of melamine, an arylsulphonamide, an aldehyde, and an alcohol are much superior to alkyd resins modified with urea resins, especially as regards gloss, stability, and tendency for films containing them to become brittle. C. O. C.

Striped Flexible Strip Material. B. F. Goodrich Co. *B.P.* 641,549.

A strip of thermoplastic material has a stripe of material deposited on it by passing it lengthways close to a nozzle from which the striping material is issuing, drying, and then heating to fuse the dried stripe into the thermoplastic strip. C. O. C.

Embossing Thermoplastic Sheet Materials. Dunlop Rubber Co. Ltd. and J. J. Hinton. *B.P.* 642,148.

Thermoplastic materials, particularly polyvinyl materials, are embossed by pressing them between a metal die and a resilient pad while they are being heated by a high-frequency electric field. C. O. C.

Polymerisable Esters. N.V. De Bataafsche Petroleum Maatschappij. *B.P.* 638,516.

Unsaturated esters of formula $R^1{\cdot}COOR^2$ (R^1 = an unsaturated radical having an olefinic linkage and R^2 = a radical containing an epoxide group), e.g. glycidyl allyl phthalate, which are polymerisable optionally in a linear or a three-dimensional manner, to yield infusible and insoluble products, are prepared by treating a salt of a compound having a carboxyl group and an olefinic linkage with a halide of an epoxy-alcohol. W. G. C.

Artificial Leather. J. Seraphim. *B.P.* 640,245.

Any type of textile fibre is immersed in an aqueous vinyl resin emulsion of any type, including acrylic resin emulsions, plasticised with casein, gluten, or an organic phthalate. If desired either or both sides of the product may then be coated with the same or another plasticised vinyl emulsion, associated preferably with a caustic reagent. C. O. C.

Arylsulphonamide-modified Melamine Resins. M. J. Scott and Monsanto Chemical Co. (III, p. 595.)

Abrasion-resistant Coatings. Du Pont. (III, p. 596.)

Copolymers of *cyclo*Pentadiene. Velsicol Corpn. (V, p. 599.)

Modified Melamine–Formaldehyde Resins. Beck, Koller & Co. (England) Ltd., T. S. Hodgins, P. S. Hewett, and A. G. Hovey. (V, p. 599.)

Ethyl Cellulose–Phenol-modified Coumarone–Indene Lacquer for Polystyrene. K. D. Bacon, A. E. Young, and Dow Chemical Co. (V, p. 600.)

Coating Sheet Material with Polyethylene Compositions. I.C.I. Ltd. and W. E. F. Gates. (X, p. 605.)

XIV—ANALYSIS; TESTING; APPARATUS

Methods of Evaluating Detergents. C. T. Snell. *Amer. Dyestuff Rep.*, 39, 485–487 (24th July 1950).

Laboratory methods for carrying out cleaning and soil redeposition tests, and for measuring surface and interfacial tension, wetting power and suspending power, which are in general use in evaluating detergents, are outlined. W. K. R.

Some Physical-Chemical Aspects of Cotton Detergency — Limitations of Present Laboratory Testing Methods. J. M. Lambert and H. L. Sanders. *Ind. Eng. Chem.*, 42, 1388–1394 (July 1950).

The methods which have been used for evaluating the efficiency of detergents in cleaning cotton goods are reviewed critically, and it is shown that they fail in many respects to simulate actual conditions of use. In most tests cotton patterns are artificially soiled with relatively large amounts of finely divided carbon black, detergency being assessed by measuring the change in reflectance after one wash. In practice, however, textiles are soiled with complex mixtures and laundered and resoiled repeatedly. The relationship between reflectance and actual soil present is not linear, and traces of ingrained soil can reduce appreciably the whiteness of the fabric. Results are described which were obtained with six detergents in multicycle wash tests in which roller towels, soiled in actual use, were washed in a domestic washing machine, detergent efficiency being assessed by laboratory reflectance measurements. These results were essentially substantiated by field tests, but patterns soiled with carbon black, included in the same washes, failed to correlate with the actual performance data. The important distinction between precision and accuracy of laboratory detergency data is emphasised, and illustrated by a typical example. W. K. R.

Colorimetric Determination of Sodium Hypochlorite. G. R. Wallin. *Text. Research J.*, 20, 514–516 (July 1950).

The method depends on the intensity of the blue colour developed when phenol, ammonium hydroxide, and sodium hypochlorite react. By holding the phenol and ammonia constant, the depth of colour formed is proportional to the amount of available chlorine present over a range of 10 mg. chlorine per 100 ml. with adherence to Beer's law.

Paper Chromatography of some Acridines. M. Lederer. *Nature*, 165, 529–530 (1st April 1950).

Absorption chromatography of vitamin A may be carried out on paper impregnated with alumina in cases where partition chromatography is unsuccessful owing to the high solubility in lipoid solvents. Separation of pairs of therapeutically active acridine dyes has been carried out by absorption chromatography on filter paper without added alumina. Development was carried out with water or aqueous HCl and good separation was obtained. No separation was obtained in partition chromatography with various solvents. W. J. M.

Spectrophotometric Measurements and the Graphical Representation of Colours. Application to White Cements. P. Janssens. *Rev. Matériaux Construction Trav. publ.*, Ed. C, No. 461, 153–162 (1950): *Chem. Abs.*, 44, 6596 (25th July 1950).

White cement has a high n and a high diffuse reflectivity. The reflectivity of an extra white, a white, and a semi-white cement was measured with a Lumetron photocolorimeter (Photovolt, U.S.A.) provided with colour filters and two photoelectric cells with $MgCO_3$ as a standard. The co-ordinates of radiation were calculated by the C.I.E. tristimulus method. Use of three special filters gave quicker results. The method is applicable to measurement of the colour of all surfaces. C. O. C.

Gloss Measurement. V. G. W. Harrison. *Paint*, 20, 277–279, 293 (Aug. 1950).

The four most important of the several factors influencing the appearance of a paint film are colour, gloss, smoothness, and texture. Broadly speaking, the colour of a paint is governed by diffuse selective reflection from pigment particles beneath the surface; it is most intense when the surface is not viewed at a specular angle. Gloss, on the other hand, is due largely to light reflected from the surface; usually this light is not coloured, and under given conditions of illumination it is concentrated near the angle of specular reflection, so that, viewed at this angle, the body colour of the paint is diluted and obscured by white "glossy" light. Gloss is also affected to a marked extent by the presence of texture or surface imperfections. Modern methods of gloss measurement are described. C. O. C.